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SOIL SCIENCE

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MATHEMATICAL RELATIONS BETWEEN TOTAL EXCHANGE CAPACITY AND ABSORPTION OF AMMONIUM AND POTASSIUM BY SOILS

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The absorption by soils of bases from salt solutions has been the subject of a great deal of study since its discovery by Way in 1849. Recently, since the clarification of ideas concerning total exchange capacity and the exchange complex, several mathematical equations have been proposed to express the relation between the total exchange capacity and the absorption of bases. The present paper gives the results of a study conducted in an effort to determine which of these various equations expresses most accurately the relation between the base exchange complex and the quantities of ammonium or potassium absorbed by soils from dilute solutions of ammonium or potassium sulfate.

EQUATIONS CONSIDERED

According to the law of mass action, the reaction between a solution of ammonium sulfate and a base exchange complex saturated with calcium can be represented by the following equation:

$$(NH_4)_2\,SO_4 + CaX_2 \leftrightarrows CaSO_4 + 2\,NH_4\,X$$

Kerr (2) applied the law of mass action to the equilibrium conditions. He assumed the active masses of the bases in the exchange complex to be proportional to their total concentrations and the ionic concentrations of ammonium and calcium as present only in the liquid phase. The equation thus developed is as follows at equilibrium:

$$\frac{(NH_4^+)^2\,(CaX_2)}{(Ca^{++})\,(NH_4X)^2} = K \qquad (A)$$

The quantities within the parentheses are active concentrations. It is assumed that the exchange complex acts as though it were in solution. K is a constant.

Vanselow (5) has suggested that instead of acting as though in solution, the base exchange compounds form a series of mixed crystals. This theory introduces another factor so that equation (A) becomes as follows:

$$\frac{(NH_4^+)^2\,(CaX_2)\,(CaX_2 + NH_4X)}{(Ca^{++})\,(NH_4X)^2} = K \qquad (B)$$

Csiky (1) quotes Vageler and Waltersdorf (4) as stating that the relation between the amounts of exchanged ions and the quantity of replacing reagent used is a very regular adsorption curve. They suggest that this curve is a hyperbola corresponding to the hyperboloid form of the dissociation residue curve, and can be characterized by the asymptote formula of the hyperbola as follows:

$$y = \frac{x \cdot S}{x + C} \qquad (C)$$

In this equation, x is the quantity of salt used, y is the quantity absorbed, S is the limiting value of the adsorption capacity, and C is the half value of the limiting value.

Patten and Waggaman (3) in 1908, stated that the absorption of potassium is closely represented by the formula

$$\frac{dy}{dv} = (A - y)$$

in which y is the amount absorbed from v cc. of solution and A is the value at the limit of adsorption. If the volume be kept constant, the concentration, x, may be introduced into the equation to give the following:

$$\frac{dy}{dx} = K(A - y) \qquad (D)$$

G. Wiegner (6) states that the relation between the quantity of an ion in solution and the quantity taken up by the soil is represented by the equation

$$y = KC^{1/p} \qquad (E)$$

in which y represents the quantity taken up by the soil, C represents the quantity in solution at equilibrium, and K and p are constants determined experimentally.

The plan of the present work was to determine the quantities of ammonium and potassium absorbed by soils varying in total exchange capacity from ammonium or potassium sulfate solutions of various concentrations, and then to use these data to test different equations already given and ascertain which most closely represented the actual process of absorption.

ABSORPTION OF AMMONIUM AND POTASSIUM

Absorption of ammonium or potassium was determined in one series, using 50 gm. of soil and 200 cc. of water containing the desired quantity of ammonium sulfate or potassium sulfate. The mixture was shaken 1 hour in an end-over-end shaking machine; preliminary experiments showed that this gave the same results as occasional shaking during 24 hours. The soil was then filtered off; ammonia was determined in the filtrate by distillation into standard hydro-

chloric acid; and potassium, by the chloroplatinate method. The solutions used contained the equivalent of 2, 4, 8, and 16 m.e. of ammonium sulfate or of 0.85, 4, and 8 m.e. of potassium sulfate per 100 gm. of soil.

The quantities of ammonium and potassium absorbed by a number of soils are given in table 1. In general, the base absorbed varied with the exchange capacity, but the relation is only approximate. The soils absorbed a little more potassium than ammonium, the average difference being 11 per cent in

TABLE 1

Ammonium absorbed from ammonium sulfate and potassium absorbed from potassium sulfate solutions of various concentrations

LABORATORY NUMBER	SOIL TYPE	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
			2 m.e.	4 m.e.	8 m.e.	16 m.e.	0.85 m.e.	4 m.e.	8 m.e.
		m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
12595	Norfolk fine sand	1.46	0.06	0.22	0.72	0.86			
12592	Norfolk fine sandy loam	2.62	0.33	0.68	1.03	1.44			
20725	Hockley fine sandy loam	3.00	0.41	0.77	1.31	1.55	0.36	0.91	1.66
12597	Susquehanna fine sandy loam	3.08	0.31	0.65	1.06	1.20	0.31	0.69	1.10
18230	Kirvin fine sandy loam	4.98	0.53	1.13	2.20	4.18			
12596	Susquehanna fine sandy loam	6.00	0.24	0.70	1.37	1.83	0.23	0.88	1.63
12647	Miller fine sandy loam	6.44	0.79	1.52	2.24	3.22			
12652	Yohola silt loam	11.30	0.91	1.73	3.04	4.65			
12518	Crockett loam	13.71	0.49	1.26	2.66	4.32	0.42	1.63	3.12
12651	Yohola silt loam	16.08	0.89	1.78	3.69	5.88			
9348	Unknown	18.31	1.18	2.30	4.19	6.80	0.67	2.46	4.51
12519	Crockett loam	18.49	0.93	1.88	3.52	5.47			
12642	Trinity fine sandy loam	18.70	0.60	1.94	3.78	5.53			
20721	Victoria clay loam	21.28	1.41	2.38	3.96	7.22			
12659	Wilson clay loam	23.43	0.97	2.18	4.03	6.66	0.54	2.39	4.06
12677	Lufkin clay loam	27.45	1.15	2.30	4.42	7.36	0.53	2.38	4.22
12581	Trinity clay	27.60	1.44	2.54	4.70	8.11	0.64	2.74	5.53
12580	Trinity clay	29.60	1.27	2.53	4.73	8.31	0.63	3.06	5.11
12533	Wilson clay loam	37.24	0.97	2.65	5.32	9.34	0.62	3.10	5.73
7147	Unknown	44.04	1.08	2.82	5.41	9.55	0.64	3.06	5.97
12571	Houston stony clay	44.13	1.17	2.73	4.73	8.28			
21067	Trinity clay	45.81	1.45	3.03	5.66	10.19	0.70	3.05	6.06
18226	Houston black clay	47.12	1.50	2.82	5.58	9.87			

the case of the 4 m.e. solution and 12 per cent with the 8 m.e. solution. It is seen from table 1 that soils of widely varying total exchange capacity absorbed similar quantities of bases; soils of similar exchange capacity absorbed different quantities of bases. The differences in absorption may be due partly to capillary adsorption and not entirely to base exchange. They suggest, however, that in the different soils, the exchange complexes are significantly different with respect to their activity of reaction with bases in the soil solution. If this

be true, it is obvious that the values of the constants in the various equations would vary significantly in different soils, and any average value would be only approximate.

In order to ascertain more definitely whether or not differences in absorption were caused by differences in the nature as well as the quantity of the exchange complex, a second series of absorption tests was made, in which a constant amount of exchange capacity was used. A quantity of each soil containing 10 m.e. exchange capacity was used with 2.5 and with 20.0 m.e. ammonium sulfate in 500 cc. of water.

The results are given in table 2. The quantity of ammonium absorbed from 2.5 me. of ammonium sulfate by 10 m.e. exchange complex varied in the different soils from 0.78 m.e. to 1.06 m.e. From 20.0 m.e. of ammonium sulfate, the quantities absorbed varied from 3.64 m.e. to 5.04 m.e. The results show significant differences in absorption, which may be due to differences in the nature of the exchange complexes of the various soils.

TABLE 2

Absorption of ammonium by quantities of soil containing 10 m.e. of exchange complex

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	WEIGHT OF SOIL USED	AMMONIUM SULFATE IN ORIGINAL SOLUTION			
			2.5 m.e.		20.0 m.e.	
	m.e.	*gm.*	*m.e.*	*per cent*	*m.e.*	*per cent*
20725	3.00	333	1.04	41.7	4.16	20.8
18230	4.98	201	1.01	40.3	4.86	24.3
12651	16.08	62.2	0.94	37.3	4.25	21.2
12642	18.70	53.4	0.78	31.0	3.64	18.2
20721	21.28	47.0	1.05	42.0	4.70	23.5
12580	29.60	33.8	1.03	41.5	4.65	23.2
12533	37.24	26.9	1.06	42.4	5.04	25.2
21067	45.81	21.8	1.04	41.7	4.68	23.4

RELATION OF RESULTS TO THE VARIOUS MATHEMATICAL EQUATIONS

The data presented in table 1 were used to calculate values in the various mathematical equations previously mentioned. The quantity of ammonium or potassium absorbed was taken to be equal to the quantity of ammonium or potassium complex formed and equal to the quantity of calcium ion in solution at equilibrium. The quantity of calcium complex was assumed to be the total exchange capacity minus the ammonium or potassium complex produced in the absorption. These assumptions are not strictly correct, but the divergences are of relatively very small importance. The various equations are discussed in the following sections.

Mass law equation of Kerr

Values of K were calculated for the equation proposed by Kerr (2),

$$\frac{(NH_4^+)^2\ (CaX_2)}{(Ca^{++})\ (NH_4X)^2} = K \qquad (A)$$

The results are given in table 3. It must be remembered that the values were calculated on the basis that the entire original exchange complex was taken up by calcium. However, small quantities of cations of a different valence were undoubtedly present and had some slight effect on the results obtained. The value of K is seen to vary widely from soil to soil, and also in the same soil with different quantities of ammonium or potassium. For many of the soils the values of K decrease with an increase in the concentration of the solution. In

TABLE 3

Calculated values of K *in the equation,* $\frac{(NH^+_4)^2\ (CaX_2)}{(Ca^{++})\ \times\ (NH_4X)^2} = K$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
		2 m.e.	4 m.e.	8 m.e.	16 m.e.	0.85 m.e.	4 m.e.	8 m.e.
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
12595	1.46	24,370.	1,664.0	105.6	186.0			
12592	2.62	178.7	68.0	70.7	83.3			
20725	3.00	95.0	52.2	33.7	81.3	14.1	26.5	14.8
12597	3.08	271.7	99.3	81.7	300.0	27.1	79.7	70.8
18230	4.98	64.6	41.8	8.8	1.5			
12596	6.00	1,261.0	168.2	79.2	136.6	229.5	73.2	38.5
12647	6.44	16.8	8.6	12.4	15.7			
12652	11.30	16.4	9.6	7.2	8.6			
12518	13.71	256.2	50.2	16.7	14.1	33.2	15.7	8.3
12651	16.08	27.3	12.5	4.6	5.2			
9348	18.31	7.0	3.8	2.7	3.1	1.9	2.8	1.8
12519	18.49	25.0	11.2	6.9	8.8			
12642	18.70	164.9	9.7	7.5	8.5			
20721	21.28	2.5	3.8	4.6	3.0			
12659	23.43	26.1	6.8	4.7	5.0	14.0	5.0	4.5
12677	27.45	12.5	6.0	3.4	3.8	18.5	4.9	4.4
12581	27.60	2.8	3.3	2.4	1.8	4.6	2.0	0.8
12580	29.60	7.4	3.5	2.5	2.1	5.6	0.8	1.5
12533	37.24	42.2	3.4	1.5	1.3	8.1	0.9	0.9
18546	38.10	9.6	2.8	1.7	1.7			
7147	44.04	28.9	2.6	3.1	1.7	7.3	1.2	0.7
12571	44.13	18.5	3.3	3.9	3.8			
21067	45.81	4.4	1.5	1.2	1.1	3.0	1.4	0.7
18226	47.12	3.4	2.8	1.4	1.5			

some soils, this decrease is comparatively small, while in others, it is very great. With a given solution, the value of K in general decreases with the increase in total exchange capacity of the different soils, but the decrease is by no means regular. The quantities of bases absorbed by soils of low exchange capacity from solutions of low concentrations are usually much too small to give satisfactory agreement with values of K calculated from solutions of higher concentrations. It is possible that under these conditions capillary absorption of the cations may be of such relative importance as to overbalance the effect of

the exchange complex. The values of K for the different soils and solutions are much greater and much more variable under the conditions previously named than with soils of high exchange capacity and more concentrated solutions.

The values of K for the absorption of potassium do not vary as much as the corresponding values for the absorption of ammonium but these, too, are very variable. They are as a rule much lower than the corresponding values for ammonium. The average increases in quantity of potassium absorbed, as compared to ammonium absorbed, were 11 per cent and 12 per cent for the 4 m.e. and 8 m.e. solutions, respectively, while the corresponding decreases in values of K were 43.7 per cent and 39.0 per cent. This shows that comparatively small differences in the quantity of base absorbed may produce large differences in values of K.

When constant amounts of exchange capacity were used (see the data in table 2), the values of K for six of the eight soils were nearly the same, averaging 17.2 for the 2.5 m.e. solution and 12.4 for the 20.0 m.e. solution. Values of K for Nos. 12651 and 12642, respectively, were 26.5 and 57.5 for the 2.5 m.e. and 19.4 and 35.3 for the 20.0 m.e. solutions. For a decrease of 25.7 per cent in ammonium absorbed from the 2.5 m.e. solution, the value of K for No. 12642 increased 334.3 per cent. This also shows the marked influence of small differences in quantity of base absorbed upon the value of K.

Kerr (2) reports results with a Hawaiian soil having a total exchange capacity of 14.77 m.e. per 100 gm. of soil. The quantities of ammonium chloride in the solutions used varied from 6.24 m.e. to 21.55 m.e., thus being considerably greater than those used in this work. For the several solutions which Kerr used, the values of K were between 12.5 and 13.3. This value is somewhat higher than that for five of the six soils in table 3 varying from 10 m.e. to 20 m.e. exchange capacity. No. 12518, a Crockett loam, gave much higher values than those of Kerr. Vanselow (5) worked with the extracted colloids of one soil and 0.1 N solution, and calculated his results to 100 gm. of colloid; the exchange capacity and the salt concentrations were equivalent to 67.5 m.e. throughout. He obtained a value of K in equation (A) of about 2.20. This value is in fair agreement with the results with ammonium reported in table 3 for the eight soils of exchange capacity over 27.5 m.e. and solutions of 8 to 16 m.e., but corresponding values for potassium are appreciably lower. The values of K obtained by equation (A) vary markedly in some soils with a variation in concentration of solution, vary widely between different soils with the same concentration of solution, and are subject to great variation with small differences in quantities of base absorbed. Consequently, equation (A) does not seem to be a good expression of the conditions involved.

Mixed crystal equation of Vanselow

The equation proposed by Vanselow (5) differs from that of Kerr by the factor $(CaX_2 + NH_4X)$:

$$\frac{(NH_4^+)^2\ CaX_2\ (CaX_2 + NH_4X)}{(Ca^{++})\ (NH_4X)^2} = K \qquad (B)$$

The values of K in table 4 are calculated by equation (B) from the data in table 2.

Vanselow used extracted soil colloids and concentrated salt solutions in his work, and consequently the suspensions were considerably different from the soils used in our work. Small differences in absorption would have comparatively much less effect on his results. On the one soil which he reports, the values of K were between 132 and 183. These values are much higher than those obtained in the present study, in which the concentrations were much

TABLE 4

Calculated values of K *in the equation,* $\frac{(NH^+_4)^2(CaX_2)(CaX_2 + NH_4X)}{(Ca^{++})\ (NH_4A)^2} = K$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM SULFATE IN SOLUTION				POTASSIUM SULFATE IN SOLUTION		
		2.0 m.e.	4.0 m.e.	8.0 m.e.	16.0 m.e.	0.85 m.e.	4.0 m.e.	8 m.e.
	m.e.							
12595	1.46	18,530.0	1,398.0	114.8	216.2			
12592	2.62	263.6	111.6	136.1	170.2			
20725	3.00	161.9	98.3	72.7	185.1	24.4	51.9	34.5
12597	3.08	460.5	185.2	169.1	642.1	46.1	150.7	148.0
18230	4.98	178.4	128.0	31.5	7.0			
12596	6.00	3,938.0	563.5	292.1	535.4	716.3	251.6	147.0
12647	6.44	60.8	34.3	53.8	76.1			
12652	11.30	100.0	62.7	51.9	69.1			
12518	13.71	1,819.0	375.8	137.1	120.5	234.3	120.2	69.7
12651	16.08	232.1	109.1	45.3	56.4			
9348	18.31	66.8	39.2	31.4	38.9	18.0	29.7	20.9
12519	18.49	242.5	114.5	75.9	105.7			
12642	18.70	1,592.0	100.4	84.6	103.3			
20721	21.28	28.0	44.5	57.4	42.8			
12659	23.43	318.9	87.2	65.6	69.5	167.5	64.3	61.8
12677	27.45	178.6	91.0	54.5	65.5	259.0	72.8	70.0
12581	27.60	39.9	49.2	38.8	32.3	65.5	29.1	13.2
12580	29.60	113.7	57.3	43.1	42.2	84.8	13.4	26.7
12533	37.24	805.4	67.6	32.4	30.0	153.9	18.7	19.6
18546	38.10	189.1	57.2	36.7	39.3			
7147	44.04	651.3	60.0	77.8	44.2	163.1	29.1	18.5
12571	44.13	418.6	76.9	97.2	98.8			
21067	45.81	104.0	35.3	32.0	31.8	68.9	33.2	17.4
18226	47.12	82.2	64.8	36.9	41.5			

lower. As with equation (A), the values of K vary with different soils, and with different concentrations of the absorbing material in the same soil.

In general, there is much less relative variation in the values of K by equation (B) than in those by equation (A). For many of the soils, the agreement between the values for a given soil for the 4, 8, and 16 m.e. solutions is fairly satisfactory; values for the 2.0 m.e. and 0.85 m.e. solutions are too high.

With soils of high exchange capacity in dilute salt solutions, the value of NH_4X is of very little importance, compared to the value of CaX_2. Under

these conditions, equation (*B*) of Vanselow amounts essentially to multiplying the value of *K* in equation (*A*) of Kerr by a constant CaX_2, the molecular concentration of the calcium exchange complex, which is equal to one-half the total exchange capacity. Equation (*B*) is then subject to the same objections as equation (*A*). On the whole, however, the introduction of the factor ($CaX_2 + NH_4X$) tends to reduce materially the variations found in equation (*A*). Equation (*B*) is therefore considered by the writer to be better than equation (*A*). It is not good in the case of dilute salt solutions because the values of *K* are found to be too high.

Possible reasons for variations in values of K *in Equations* (A) *and* (B)

The variations in the values of *K* presented in tables 3 and 4 may be due to a number of reasons. The simplest is perhaps of a mathematical nature, and holds where the quantity absorbed is less than 1. The square of this fraction is less than the original quantity. Since the square is used in the denominator of both equations (*A*) and (*B*), the resulting quotient will be larger than in cases where the original quantity is greater than 1. This increases the effect of small errors and might account for much of the apparently great variation of *K* with dilute solutions and soils of low exchange capacity.

A second reason may be found in differences in the nature of the exchange complexes of different soils. Such differences have already been suggested (table 2). Moreover, the exchange complex in a single soil may contain compounds which vary considerably in reactivity with bases in the solution. Consequently, at one level of reaction with a given base, a certain part of the exchange complex may be the principal absorbing compound, whereas at another level, a different compound may be the principal one, with a different state of equilibrium between soil and salt solution. It is also possible that we are dealing in this case with a complex saturated with various cations, including hydrogen ions.

The great effect of small variations in quantity of base absorbed upon the values of *K* has already been mentioned. Quantities of ammonium or potassium which are certainly within the range of experimental error are sufficient to cause considerable variation in the value of *K* when the total quantity absorbed is small, especially with dilute solutions and soils of low exchange capacity, where the principal variations of *K* occur. Experimental error may therefore be an important factor.

Another cause of variations in quantities of base absorbed is undoubtedly hydrolysis of the exchange complex. The total quantity of base absorbed is the result of an equilibrium between two reactions. The first is between the calcium complex and the base in the solution; the second is between the ammonium complex formed and the water as such or containing carbon dioxide:

$$NH_4X + H_2O + CO_2 = NH_4HCO_3 + HX$$

A number of experiments were conducted in order to determine some of the factors involved in hydrolysis.

Hydrolysis of the ammonium complex

The relation between the total exchange capacity of various soils and the quantity of ammonium removed by hydrolysis was first determined.

Soils varying from 2.6 to 39 m.e. in exchange capacity were selected and were completely saturated with ammonium. Ten grams were leached with 250 cc. of neutral normal ammonium acetate. The excess ammonium acetate was then washed out of the soil with ethyl alcohol. It was very difficult to be certain that all of the excess amonium had been removed, since the presence of alcohol greatly reduced the sensitivity of the Nessler test. Although a slight excess of ammonium might not be significant in the estimation of total exchange capacity, it was of great importance in this experiment where very

TABLE 5

Ammonium hydrolyzed from soils previously treated with ammonium salt solutions in ways indicated

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM HYDROLYZED FROM COMPLEX SATURATED WITH AMMONIUM		AMMONIUM ABSORBED AND HYDROLYZED FROM SOILS TREATED WITH 2 M.E. $(NH_4)_2SO_4$ SOLUTION		
				Absorbed	Hydrolyzed	
	m.e.	*m.e.*	*per cent*	*m.e.*	*m.e.*	*per cent**
12592	2.62	0.59	22.4	0.33	0.40	121
20724	4.13	0.50	12.1	0.35	0.26	80
18230	4.98	0.76	15.2			
12596	6.00	0.90	15.0	0.24	0.24	100
18539	12.69	0.82	6.5			
9347	18.13	1.38	7.6	1.00	0.37	37
12519	18.49	1.46	7.9	0.93	0.54	58
12642	18.70	0.66	3.5	0.60	0.46	77
20721	21.28	0.96	4.5	1.41	0.51	36
21071	26.38	1.00	3.8	1.25	0.40	32
12677	27.35	1.02	3.7	1.15	0.53	46
21072	38.80	1.00	2.6			

* Per cent of that absorbed.

small quantities of ammonium were involved. On the other hand, excessive washing might cause some hydrolysis with removal of some of the ammonium combined with the exchange complex. No satisfactory test for the determination of the end point of the washing was developed. The soil was washed with alcohol three or four times after a negative Nessler test, transferred to bottles, and 40 cc. of ammonia-free water added. The bottles were shaken for 1 hour on an end-over-end shaking machine. The soil was then filtered off, and ammonium was estimated in an aliquot of the filtrate by the Nessler method.

The results are given in the third column of table 5. The quantity of ammonium in solution varied with different soils but the increase was not in direct proportion to the exchange capacity of the soil. After the total exchange capacity exceeded 6 m.e., the ammonium in solution was almost constant,

being about 1 m.e. The percentage of ammonium hydrolyzed decreased from 22.4 to 2.6 as the exchange capacity increased. These results strongly indicate that the quantity of ammonium brought into solution by hydrolysis of the base exchange complex may be related more closely to the volume of the water present than to the base exchange capacity.

Another test was made to ascertain the amount of hydrolysis when only part of the bases of the exchange complex were replaced by ammonium.

Two 10-gm. samples of nine soils were shaken for 1 hour with 40 cc. of solution containing ammonium sulfate equivalent to 2 m.e. per 100 gm. of soil. The solution was then filtered off and the soil washed free of excess ammonium sulfate with ethyl alcohol. The samples were then suspended in 40 cc. of ammonia-free water, shaken for 1 hour, filtered, and the ammonium in solution determined by the Nessler method. The results are presented in the last columns of table 5. The quantities of ammonium absorbed are to some extent related to the exchange capacity of the soils. The quantity of ammonium removed from the soil by hydrolysis was nearly constant, especially with the last six soils in the table, although the total exchange capacity and the quantity of ammonium absorbed varied considerably. Perhaps the most interesting soil in this connection is No. 12642. Although it absorbed considerably less ammonium than could have been expected from the total exchange capacity, the quantity of ammonium from this soil by hydrolysis is practically the same as for the other soils.

A third experiment was conducted in which a constant amount of 1.0 m.e. of exchange complex was used from different soils. The same soils were used as those listed in table 2, but only 10 per cent as much. In all but two of the soils, the quantity of ammonium hydrolyzed was practically identical, varying from 1.13 to 1.35, and averaging 1.23 m.e., or 12.3 per cent of the total present. Soils 12642 and 20721 gave low results, 0.96 m.e. and 0.93 m.e. respectively.

The effect of the volume of water upon the hydrolysis of the base exchange complex was tested because the volume of water was apparently of importance. The base exchange complexes of 10-gm. lots of soils Nos. 12596, 18539, 12642, and 20721 were saturated with ammonium from ammonium acetate as has been described, washed, and shaken with 20, 40, 80, and 160 cc. portions of water. The m.e. of ammonium in solution were as follows: for 20 cc. of water, 0.82, 0.71, 0.78, and 0.80; for 40 cc. of water, 0.90, 0.82, 0.66, and 0.98; for 80 cc. of water, 1.30, 1.24, 1.40, and 1.35; for 160 cc. of water, 1.38, 1.20, 2.81, and 2.59. For the first two volumes, the amount of ammonium hydrolyzed was practically identical for all the soils. With the 80 cc. of water, the ammonium hydrolyzed was appreciably higher than with the 20 cc. or 40 cc. With the 160 cc., or a ratio of 1:16, solutions from soils Nos. 12642 and 20721 contained twice as much ammonium as those from Nos. 12596 and 18539.

The results presented show that hydrolysis occurs and that it plays a relatively more important rôle with soils of low exchange capacity than with those of high exchange capacity. When the quantity of base in the salt solution is

low, the quantity hydrolyzed may be relatively large when compared with the total quantity absorbed by the soil. A part of the variations in the values of the constant K in equations (A) and (B) is undoubtedly due to hydrolysis.

Adsorption equation of Csiky

The three equations now to be considered are based upon adsorption, instead of equilibrium in accordance with the mass law upon which equations (A) and (B) are based. The first of these is that proposed by Vageler and Woltersdorf (4) and Csiky (1):

$$y = \frac{x \cdot S}{x + C} \qquad (C)$$

where $x =$ the quantity of reagent used for ion exchange, $y =$ the exchanged ions found, $S =$ the limiting value of the absorption capacity. If reciprocal values are used, the graph becomes a straight line, of the formula

$$\frac{1000}{y} = \frac{1000}{S} + q\,\frac{1000}{x}$$

where q is the slope of the curve, determined by the data of two determinations with solutions of different concentrations, which give two points on the curve. The values for q and S were calculated from data presented in table 1, and are given in table 6. The values for q are fairly constant in practically all of the soils. The agreement between the several values is much better than that for K in either equation (A) or (B). However, the value of q is somewhat variable for soils of low exchange capacity and dilute solutions. The quantities absorbed are still too small to fulfill the requirements of equation (C).

The values of S were calculated for the value of q between 8 and 16 m.e. of ammonium sulfate, and the values of x and y for 16 m.e. The values of S represent the limiting values of the absorption capacity. They are presented in the fifth column of table 6 with the total exchange capacities for comparison in the sixth column. The agreement between the value of S and the total exchange capacity is fairly good for 18 of the 24 soils, but not so good with the other 6. In many cases, the agreement between the calculated value and the laboratory determination is within the range of experimental error.

In order to estimate the magnitude of the variation of values of q and S with dilute solutions, the values of y when $x = 2$ were calculated from the data for $x = 16$; the determined values of y were subtracted from the calculated values of y. The differences are given in the last column of table 6. In most cases, the differences are small and within the experimental error.

Values of q and S for the potassium data are also given in table 6. The values of q vary from 1.20 to 3.54 but are somewhat more constant than those for ammonium. Values of S for most of the soils agree closely with the values for total exchange capacity, but in soils Nos. 12533 and 7147, they are much too large.

Values of q for the data presented in table 2 (absorption of ammonium by a constant quantity of exchange complex) varied from 2.06 to 2.88, with an average of 2.36. Values of S varied from 7.15 (No. 12642 with very low absorption of ammonium) to 10.84, the average being 9.08, instead of the 10.0 used.

TABLE 6

Values of q, S, *and* y *in the equation* $\frac{1000}{y} = \frac{1000}{S} + q\frac{1000}{x}$

LABORATORY NUMBER	q Ammonium			q Potassium	S FOR AMMONIUM	TOTAL EXCHANGE CAPACITY	S FOR POTASSIUM	DIFFERENCE BETWEEN CALCULATED AND DETERMINED VALUE OF y
	2–4 m.e.	4–8 m.e.	8–16 m.e.	0.85–8.0 m.e.				
						m.e.		
12595	48.48	25.25	3.65		1.07	1.48		0.30
12592	6.24	4.00	4.04		2.26	2.62		0.08
20725	4.56	4.26	1.89	2.06	5.01	3.00	2.91	0.08
12597	6.75	4.76	1.76	2.20	1.40	3.08	1.54	0.31
18230	4.00	3.44	3.45		4.25	4.98		0.02
12596	10.96	5.34	2.93	3.54	2.76	6.00	5.81	0.30
12647	2.43	1.69	2.17		5.71	6.44		0.00
12652	2.08	1.99	1.82		9.87	11.30		0.09
12518	5.01	3.34	2.31	1.96	11.48	13.71	13.25	0.32
12651	2.25	2.33	1.62		14.56	16.08		0.25
9348	1.65	1.57	1.47	1.21	18.12	18.31	14.10	0.08
12519	2.17	1.98	1.62		12.27	18.49		0.19
12642	4.60	2.01	1.34		10.34	18.70		0.71
20721	1.52	1.51	1.49		22.03	21.28		0.00
12659	2.25	1.69	1.57	1.53	19.19	23.43	17.85	0.22
12677	1.74	1.67	1.45	1.57	22.08	27.35	24.40	0.15
12581	1.21	1.45	1.43	1.32	29.67	27.60	30.30	0.12
12580	1.57	1.47	1.45	1.32	34.48	29.60	32.25	0.06
12533	2.61	1.52	1.29	1.37	37.74	37.24	250.00	0.52
18546	1.68	1.48	1.31		38.17	38.10		0.20
7147	2.29	1.36	1.28	1.33	42.55	44.04	143.0	0.43
12571	1.95	1.24	1.47		36.50	44.13		0.14
21067	1.44	1.23	1.26	1.20	51.30	45.81	66.6	0.09
18226	1.25	1.40	1.26		44.20	47.12		0.03

Equation (*C*) gives fairly constant values of q for all soils; the values of S agree fairly well in nearly all soils with the total exchange capacity and with the quantities of ammonium and potassium absorbed. It appears to be a fairly satisfactory equation.

Absorption equation of Patten and Waggaman

On the basis of early work, conducted before the development of modern concepts concerning exchange capacity, Patten and Waggaman (3) suggested

that the absorption of a base by a soil followed a curve which may be expressed by the differential equation:

$$\frac{dy}{dv} = K(A - y) \qquad (D)$$

Upon integration and changing to Briggsian logarithms, equation (D) becomes

$$\text{Log } (A - y) - \log A = -Kv.$$

TABLE 7

Values of 1000 K *in the equation* $\frac{dy}{dx} = K(A - y)$

LABORATORY NUMBER	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
	2 m.e.	4 m.e.	8 m.e.	16 m.e.	0.85 m.e.	4 m.e.	8 m.e.
12595	9.2	17.8	36.9	24.1			
12592	29.3	32.6	27.1	21.7			
20725	31.4	32.2	31.1	19.7	49.7	39.3	32.2
12597	23.1	25.7	22.9	13.4	54.2	27.6	24.0
18230	24.4	27.9	31.7	49.6			
12596	8.9	13.5	14.1	9.8	20.0	17.2	17.3
12647	28.1	29.2	23.2	18.8			
12652	18.3	18.1	17.0	15.7			
12518	7.9	10.5	11.7	10.3	15.6	11.2	14.0
12651	12.4	12.8	14.2	12.6			
9348	14.3	14.6	14.1	12.6	19.0	15.7	15.4
12519	11.0	11.7	11.5	9.5			
12642	7.1	11.9	12.3	9.5			
20721	15.0	12.9	11.2	11.2			
12659	9.2	10.6	10.3	9.1	12.0	11.8	10.3
12677	9.3	9.5	9.5	8.5	10.0	9.5	9.1
12581	11.7	10.5	10.1	9.5	12.1	11.4	2.1
12580	9.5	9.7	9.5	9.0	10.9	11.8	10.3
12533	5.8	8.0	8.4	7.8	8.6	11.9	9.1
18546	7.3	8.1	8.1	7.6			
7147	5.4	7.2	7.1	6.7	7.5	7.8	7.7
12571	5.8	6.9	6.2	5.7			
21067	7.0	7.9	7.2	6.9	7.9	7.5	7.7
18226	7.0	7.9	7.5	6.7			

If the volume be kept constant, the term v may be replaced by the concentration, x, of the solution used. The equation states that the rate of change in quantity absorbed with the change in quantity of salt used is proportional to that part of the exchange complex not already combined with the base concerned. Values of K calculated for the data given in table 2 are given in table 7.

The values of K for soils of low exchange capacity are relatively high. For the same soil, there is very good agreement in the values of K for solutions of

different concentrations. The values for potassium are very similar to those for ammonia, indicating that minor differences in absorption are not greatly magnified in this equation. The values of K vary with different soils, tending to decrease as their exchange capacity increases.

Adsorption equation of Wiegner

The relationship between the concentration of an ion in the solid phase—the soil—and the concentration in solution at equilibrium has been held by G. Wiegner (6) to be identical with the Freundlich adsorption equation:

$$y = KC^{1/p} \qquad (E)$$

where y is the amount in unit weight of soil, including that originally present, C the concentration of the ion in solution, and K and p are constants. By changing equation (E) from the exponential to the logarithmic form, the following equation is obtained:

$$\text{Log } y = \text{Log } K + 1/p \log C.$$

This is a straight line equation in which log y is plotted against log C, K is the quantity of ammonia adsorbed when $C = 1$, and $1/p$ is the slope of the curve so constructed. Curves were constructed on this basis. In practically all soils, the values as plotted fell on a smooth curve, so that it was possible to interpolate accurately for the values of K and calculate those of p. Values of K and p are given in table 8.

In equation (E), no account is taken of the total exchange capacity, since the only variables are the quantities of the ion absorbed and that in solution. If the value of K, that is, the total quantity in the soil at unit concentration in solution, be divided by the number of units of total exchange capacity, T, the result will be the quantity of ion taken by a unit of exchange capacity when a unit of ion is in solution. This is perhaps one of the best possible ways of obtaining comparative data for the absorption reactivity of the complexes of different soils. This quantity was calculated and is given in the fourth and ninth columns of table 8. The values of K/T differ considerably in the various soils and also for ammonium and potassium. An average of the same 12 soils gave K/T a value of 0.0620 with ammonium and 0.0851 with potassium. The value of p was practically constant with all of the soils; there was no difference between ammonium and potassium in this respect. By using the average values, equation 4 can be changed to read

$$y = .0648\ T\ C^{.77} \text{ (ammonium)}$$
$$y = .0851\ T\ C^{.77} \text{ (potassium)}$$

In cases where the final concentration is low, the exponent is so nearly 1 that it is of comparatively little importance. If it be disregarded, equation (E) may be used to calculate the quantity of ammonium which would be absorbed when a given amount, B, is applied to the soil. Under conditions similar to

those in the experimental work reported in this paper, equation (E) may be rearranged to give:

$$y = \frac{.0648\ T\ B}{1 + .0648\ T}.$$

With this equation, y was calculated for ammonium when $B = 2$ and (by the use of $.0851T$ instead of $.0648T$) for potassium when $B = 0.85$. The calculated

TABLE 8

Calculated values of constants in equation $y = KC^{1/p}$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY (T)	AMMONIUM			AMMONIUM ABSORBED FROM 2 M.E. SOLUTION		POTASSIUM			POTASSIUM ABSORBED FROM 0.85 M.E. SOLUTION	
		K	$K/T \times 100$	P	Calculated	Found	K	$K/T \times 100$	P	Calculated	Found
					m.e.	*m.e.*				*m.e.*	*m.e.*
12595	1.46	0.025	1.73	1.20	0.17	0.06					
12592	2.62	0.25	9.54	1.45	0.29	0.33					
20725	3.00	0.30	9.99	1.60	0.33	0.41	0.54	18.00	1.75	0.18	0.36
12597	3.08	0.29	8.97	1.45	0.33	0.31	0.41	13.30	2.15	0.18	0.31
18230	4.98	0.36	7.24	1.05	0.49	0.53					
12596	6.00	0.23	3.93	1.10	0.55	0.24	0.34	5.66	1.20	0.30	0.23
12647	6.44	0.49	7.62	1.10	0.59	0.79					
12652	11.30	0.91	8.00	1.25	0.85	0.91					
12518	13.71	0.39	2.85	1.20	0.94	0.49	0.86	6.25	1.15	0.47	0.42
12651	16.08	0.91	5.64	1.25	1.02	0.89					
9348	18.31	1.38	7.56	1.30	1.04	1.18	2.00	10.91	1.55	0.53	0.67
12519	18.49	0.98	5.30	1.25	1.09	0.93					
12642	18.70	1.36	7.30	1.55	1.09	0.60					
20721	21.28	1.91	9.01	1.65	1.16	1.41					
12659	23.43	1.32	5.68	1.25	1.21	0.97	1.35	5.75	1.30	0.58	0.54
12677	27.45	1.41	5.09	1.10	1.27	1.15	1.39	5.05	1.20	0.61	0.53
12581	27.60	2.08	7.58	1.40	1.28	1.44	2.46	8.93	1.15	0.61	0.64
12580	29.60	2.09	7.12	1.50	1.31	1.27	2.14	7.23	1.05	0.62	0.63
12533	37.24	2.08	5.61	1.05	1.42	0.97	2.53	6.78	1.05	0.65	0.62
18546	38.10	2.24	5.82	1.35	1.44	1.27					
7147	44.04	2.38	5.41	1.15	1.45	1.08	2.88	6.55	1.05	0.68	0.64
12571	44.13	2.32	5.40	1.60	1.48	1.17					
21067	45.81	3.01	6.57	1.40	1.51	1.45	3.62	7.67	1.15	0.69	0.70
18226	47.12	2.64	5.60	1.40	1.51	1.50					
Average (24 soils).....		1.31	6.48	1.32	0.99	0.89					
Average (12 soils).....			6.20	1.30	1.05	0.91		8.51	1.31	0.51	0.53

quantities, compared with those found by experiment, are given in four columns of table 8 under the respective headings of ammonium and potassium. In most cases, the differences between "calculated" and "found" are within the experimental error. The average quantity of ammonium calculated was 11 per cent greater and the average potassium 4 per cent smaller than that found.

Equation (E) gives values which agree excellently with the experimental data. It is a good method for comparing quantitatively the absorption capacity of the exchange complexes of different soils. For practical use and without regard to the theories involved, equation (E) is probably the best of all of the equations studied.

SUMMARY

Five mathematical equations expressing the relations between total exchange capacity and the absorption by soils of ammonium and potassium from solutions of ammonium sulfate and potassium sulfate were studied in order to determine which equation gave values in best accordance with experimental results. The results of the study may be summarized as follows:

Quantities of base absorbed varied approximately with the total exchange capacity. However, marked differences were evident in the quantity of base absorbed by soils of similar exchange capacity from identical solutions. These were probably due to the relative importance of capillary absorption and to differences in the compounds making up the exchange complex.

The simple mass law equilibrium equation, $(NH_4^+)^2\,(CaX_2)/(Ca^{++})\,(NH_4X)^2 = K$, gave values for the proportionality constant, K, which were too high with soils of low exchange capacity and solutions of low concentration.

The mass law equilibrium equation in which the theory of mixed crystals is introduced, $(NH_4^+)^2(CaX_2)(CaX_2 + NH_4X)/(Ca^{++})(NH_4X)^2 = K$ gave somewhat better agreement between the values of K than the preceding equation, but was not good with some of the conditions under which the simple mass law equation held.

Values calculated for the adsorption equation $y = xS/(x + C)$ were comparatively uniform. Values of y as calculated agreed fairly closely with the quantity of ammonium absorbed. Values of S, the adsorptive limiting value of the equation, agreed fairly well with the total exchange capacity. The equation is fairly satisfactory.

Values of K calculated according to the differential equation $dy/dx = K(A - y)$ were fairly uniform for a given soil and solutions of different concentrations. The values were somewhat higher with soils of low exchange capacity.

The equation $y = KC^{1/p}$ gave values which are in best accord with the values determined experimentally. The value of K, when divided by the total exchange capacity, T, gave a quotient which was fairly similar for all soils. It indicated, however, significant differences in the absorptive capacity of some soils per unit of exchange complex. The values of p were practically constant for all soils. The equations best fitting the general data were $y = .0648\,TC^{.77}$ for ammonium and $y = .0851\,TC^{.77}$ for potassium.

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SOIL TEMPERATURE APPARATUS FOR FIELD WORK

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In connection with some work on the development of grasshopper eggs in nature, during the unseasonably warm spring of 1934, the writer had occasion to collect many soil temperature data. It was, of course, necessary to leave the ground undisturbed in order to obtain accurate temperature readings. Some of the readings made on shaded slopes involved the penetration of frozen surface soil in which the usual types of soil thermometer could only be employed with difficulty. Furthermore these soil thermometers could not be readily used for temperatures at depths below six inches. For these reasons a thermocouple constructed as described was found to be most satisfactory.

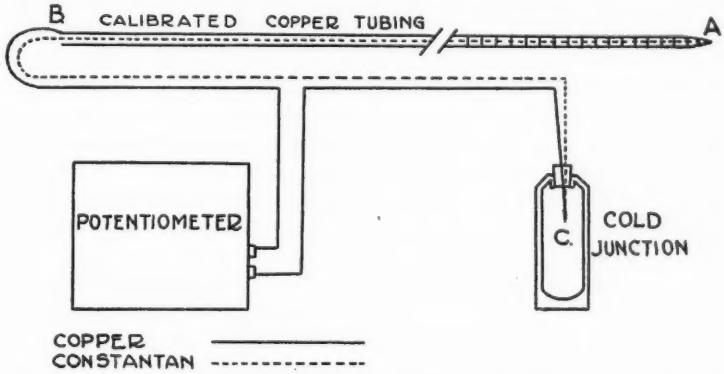

FIG. 1. SOIL TEMPERATURE APPARATUS

A piece of thick-walled copper tubing having an outside diameter of $\frac{3}{16}$ inch and 15 inches in length was hammered out to a taper point. A well-insulated 28-gauge constantan wire was drawn through the tube, and its end was welded to the tapered point (A) as illustrated (fig. 1). The tube was then filled with insulating compound. To the other end of the tube was soldered an insulated 28-gauge copper wire (B). The copper and constantan wires were encased in rubber tubing for a foot or two beyond the copper tubing as a measure of protection. Beyond the rubber tubing a second thermocouple (cold junction) was made (C), and the set-up was ready for use with a potentiometer. By filing half or quarter inch divisions on the tube, it could be readily forced

into the ground to any desired depth within its range and the temperature at its tip be quickly recorded.

The thermocouple potentiometer used in the field was a General Electric type PJ-1B. As this particular instrument has a built-in galvanometer and a temperature compensator it is unnecessary to carry an outside galvanometer or a thermos flask of cracked ice for the cold junction, but these might be needed with some makes of galvanometers such as the Leeds and Northrup Pyrovolter.

With this apparatus it is possible to measure a temperature gradient in most situations involving soil temperature much more speedily than is possible by the use of the standard soil thermometer in general use.

CORROSIVENESS OF CERTAIN OHIO SOILS[1]

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Recognition of the fact that pipe lines laid in certain areas are seriously corroded by contact with the soil, while in other areas they are relatively unaffected, has resulted in the development of a variety of methods for predicting the corrosive action of soils. The procedure usually followed in these methods consists in testing the soil in place at more or less arbitrary intervals along a right-of-way, and in indicating from the results those sections where corrosion will be severe and hence where protection of the pipe line will be required. Instead of testing the soil in place, samples of soil may be taken at definite points and examined in the laboratory. In either procedure, no effort is made to classify and to fix the boundaries of the types of soil which occur along the prospective pipe line.

For a corrosion survey to have wide application and to be made economically, the determination of the corrosiveness of each soil type is essential. Once the corrosiveness of each soil type has been definitely established, the extent of corrosion that will probably be encountered along a pipe line passing through these soils can be estimated by identifying the soils and fixing their boundaries. The purpose of this study was to determine whether the corrosiveness of certain soil types is sufficiently well defined to be of practical use in corrosion surveys. If so, it should be possible to estimate the corrosiveness of other soils by correlating certain properties of the soil types with their corrosiveness.

SOURCE OF CORROSION DATA

The field work of this investigation was conducted along the right-of-way of a group of parallel pipe lines in northern Ohio. A correlation between the repairs which have been made on a 32-mile section of these lines and the eight types of soil occurring along the lines has been previously shown by one of the authors (1). In the present study the scope of this preliminary work was extended to approximately 200 miles, and the number of soil types identified was increased to 35.

[1] The investigation of pipe line corrosion, of which the work described in this paper is a part, is a project of the American Gas Association. The staff of the National Bureau of Standards coöperated in certain phases of the work.

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Data on the corrosiveness of the soils were obtained from the record of repairs made on the pipe lines from the time of their installation to the present, a period of approximately 45 years. This record is based upon the actual leaks which have occurred in operating the lines. When a leak occurs it is repaired temporarily and the exact location and date of repair is recorded. Experience has shown that when several leaks have occurred on a short section of the line more leaks can be expected and that they will occur with increasing frequency. Finally, when the accumulation of leaks indicates the necessity of reconditioning, the pipe is uncovered and repaired by spot welding the pits and patching the larger corroded areas. The repair crew then works along the line in both directions until in the judgment of the foreman further uncovering and repair work are unnecessary. The fact that most of the reconditioning was done on short sections, *e.g.*, a few hundred feet, indicates that the work was done only when necessary. Although the repair record can not be considered a precise measure of the corrosion that has occurred, it has the advantage of a long time experiment, in which the effects of seasonal variation and accidental causes of failure, such as defective pipe, are minimized.

DESCRIPTION OF SOILS

In the extreme western part of Ohio the pipe lines are in the region of glacial limestone soils, the Clyde, Brookston, Crosby, and Miami soils being the most widely distributed along the lines. Proceeding eastward, the lines enter the glacial lake region of northwestern Ohio, in which the soils are derived from both glacial and lacustrine material. In this region the soils could be readily classified in well-recognized series with the exception of certain soils which, although similar to the Wauseon soils, differed from the latter in having a yellowish brown heavy subsoil instead of the darker sandy subsoil typical of the true Wauseon. Because of this difference and also the fact that glacial till occurred at a relatively shallow depth (24 inches) the soils were tentatively classified as "Wauseon-like" soils.

The pipe lines in the eastern part of Ohio lay wholly in the region of glacial soils derived from sandstone and shale. The predominant glacial soils in this region belong to the following series: Wooster, Canfield, Ellsworth, Mahoning, and Trumbull. The terrace and flood plain soils occurring most extensively are those of the Chenango, Braceville, Chagrin, and Holly series.

METHODS

Field work

The field work consisted in identifying and mapping the soil types along the pipe lines. Borings were made where there was any question as to the soil type, and samples were taken when necessary, depending largely upon the variations that were found in the soils. At many locations a sample was taken of the soil in each horizon of the profile to a depth of 30–36 inches. Usually, however, a single sample was taken from the middle or B-horizon in which the pipe lines were usually found. The soil types were indicated on the topo-

graphic map with appropriate symbols, and features which appeared to be significant were recorded in the notes. Distances from known stations were measured by pacing. About 8 miles of line per day could be surveyed in this manner. In order to avoid the possibility of bias in mapping the soils the record of repairs was not examined until after the completion of the survey.[2]

Estimation of total acidity of soils

The laboratory work was limited to measurements of the total acidity and resistivity, since these properties appear to be most closely related to the corrosiveness of soils (3, 4). The acidity was measured by a modification of the titration method described by Denison (2). A 5-gm. portion of the air-dry soil, which had been passed through a 20-mesh sieve, was placed in each of two test tubes (25 × 200 mm.) and 25 ml. of *N* NaCl solution was added to each tube. One milliliter of 0.2 *N* Na_2CO_3 was pipetted into one tube and 2 ml. into the other. The pH of the solution in the more alkaline tube was then determined colorimetrically, cresol red being used as the indicator. If the pH was below 7.2, the lower limit of the indicator, 2 ml. more of the carbonate solution was added to each tube and the process was repeated until the pH of the more alkaline solution was above 8. The tubes were allowed to stand with occasional shaking until the solutions were in equilibrium with the soil and showed no further change of pH with time. The amount of alkali required to bring the soil to pH 8 was then determined by interpolation or extrapolation, the titration curve being assumed to be a straight line for the short distance between the two pH values. For a 5-gm. sample, 1 ml. of 0.2*N* Na_2CO_3 solution is equivalent to 4 m.e. of hydrogen ion per 100 gm. of soil. The titration was made to pH 8 because the points of inflection in the titration curves for a large number of soils were found to be near this value (2). Although the results by this method are not accurate to better than 1 m.e. of acid per 100 gm. of soil, they are sufficiently close for the purpose, because acidity measurements of samples taken adjacent to each other in the field frequently vary by more than this amount.

From the values for acidity and resistivity of the individual samples the average acidity and resistivity of each soil type was calculated. In the case of those locations in which samples were taken from the different horizons, the average acidity and resistivity of the horizons, weighted according to their thickness, were used in computing the average values for the soil types.

PROPERTIES AND CORROSIVENESS OF SOIL TYPES

The total acidity and resistivity of each soil type together with the approximate standard deviations of the means[3] are shown in table 1.

[2] The authors are indebted to Dr. G. W. Conrey of the Ohio Agricultural Experiment Station and to Mr. A. E. Taylor of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for suggestions concerning the identification of the soils.

[3] Standard deviation of the mean = $\sigma M = \frac{\sigma X}{\sqrt{n-1}}$ (approximately) where σX = standard deviation of individual results, σM = standard deviation of mean = standard error, n = number of observations.

It is apparent from the magnitude of the standard deviations of the mean and from the numbers of samples that the average values given for the different

TABLE 1

Summary of soil acidity and resistivity measurements

SYMBOL AND SOIL TYPE	NUMBER OF SAMPLES	ACIDITY (M.E. PER 100 GM.)		RESISTIVITY (OHM-CM. AT 60°F.)	
		Mean	Standard deviation of mean	Mean	Standard deviation of mean
A_1 Clyde clay loam 1st section	13	14.6	1.5	2,758	224
A_2 Clyde clay loam 2nd section	3	14.0	1.9	2,983	112
B Braceville loam	2	15.0	...	9,410	...
Bc_1 Brookston clay loam 1st section	25	14.2	0.9	3,051	215
Bc_2 Brookston clay loam 2nd section	7	14.0	2.7	2,965	600
C Caneadea silt loam and fine sandy loam	8	12.7	2.1	4,329	837
Ca Canfield silt loam	7	18.7	1.6	9,773	1,037
Ch Chagrin Silt loam and fine sandy loam	15	12.6	1.0	6,184	675
Ci Cinders	6	14.6	4.0	2,081	160
Cs_1 Crosby silt loam 1st section	19	22.0	1.2	4,337	260
Cs_2 Crosby silt loam 2nd section	2	19.0	...	5,660	.....
D Chenango silt loam	2	9.5	...	8,320	.....
E Ellsworth silt loam	5	20.4	2.5	7,134	1,880
G Genesee silt loam	7	7.3	1.0	2,661	512
H Holly clay loam	10	26.7	2.4	3,100	763
K Lorain fine sandy loam	1	7.0	...	4,400	.....
Kc Lorain clay loam	5	14.0	3.2	3,489	321
L Lordstown fine sandy loam	2	16.5	...	11,450	.....
Ll Millsdale and other shallow limestone soils	..	....	...	.....	.....
Lf Lucas fine and very fine sandy loams	2	6.7	...	7,210	.....
M Mahoning silt loam	37	18.1	0.7	4,903	475
Ms Miami clay loam, silt loam, and fine sandy loam	17	16.8	2.8	3,982	452
Mu Muck	1	36+	...	2,070	.....
N Nappanee clay loam	3	17.5	3.6	1,009	350
Nf Newton fine sandy loam	1	8.0	...	2,820	.....
P Plainfield fine sand includes gravelly phase	2	6.7	...	6,720	.....
S Undifferentiated sands and sandy loams	1	8.0	...	2,990	.....
T Trumbull clay loam and silt loam	8	21.1	2.3	4,455	720
Ti Till (some Allis and Chenango)	6	9.3	5.6	2,525	920
V Volusia silt loam	30	17.2	1.0	5,473	383
Vl Volusia loam	5	10.4	1.3	6,023	603
Wf Wooster fine sandy loam	2	14.7	...	6,442	2,718
Wl Wooster loam	13	15.5	1.6	8,002	1,010
W Wauseon fine sandy loam	2	7.5	...	4,248	.....
Wa "Wauseon-like" soils	1	8.0	...	694	.....

soils are not equally reliable. Thus the average acidity and resistivity of an extensive soil type, such as the Mahoning silt loam, is known with a high degree of precision because a large number of samples of such soils were taken. On

the other hand, little reliance can be placed upon the values for soils present to a limited extent along the pipe line, since they are represented by so few samples.

It will be noted that the data for three soils; namely, the Clyde clay loam, the Brookston clay loam, and the Crosby silt loam, have been separated into two groups for which, however, the respective acidities and resistivities are practically the same. This separation was suggested by the fact that the extent of repairs differs greatly in areas of each of these soil types depending upon their position with respect to a certain division point on the pipe line. West of this division point, where the soils are more corrosive, the pipe lines parallel a railroad for many miles. It is possible that the accumulation of cinders on the surface of the soils might account for their greater corrosiveness in this region.

The essential data on the corrosion of the pipe lines are given in table 2. The repairs which have been made in the different soils are expressed both as percentage per area and percentage of the total length of line in each soil type. According to the first method of expressing the data the repairs in the various bodies are simply averaged without regard to the size of the area. The standard deviation of the percentage of pipe repaired in each type (column 4) was obtained by weighting the percentages for each separate area according to the length of line in that area. The standard deviation of the mean (column 8) was also calculated for the separate areas. Since this value varies inversely with the square root of the number of observations it does not give a true idea of the accuracy of the mean in the case of those soils which occurred in a few large bodies.

The data of table 2 show that although there is considerable spread in the amount of pipe replaced in various areas of the same soil type, there are consistent differences in the corrosiveness of the various types. Thus among the most corrosive soils must be listed the Clyde clay loam 1st section (A_1), soil overlaid by cinders (Ci), the Nappanee clay loam (N), and the "Wauseon-like" soils (Wa). On the other hand, the Canfield (Ca), Lordstown (L), and Wooster (Wl) silt loams and the large group of undifferentiated sands and sandy loams (S) must certainly be considered non-corrosive. The certainty with which the corrosiveness of the different soils is known depends upon the extent to which the soils occur along the pipe lines. For instance, relatively little weight can be given to the value for the Lorain fine sandy loam (L) since only one-half mile of this soil was mapped.

Further examination of table 2 shows that the repairs in small bodies of a given soil type are more likely to differ from the average of that type than are the repairs in larger bodies. It will be observed that in general the standard deviations of the percentage repaired per body of soil (column 7) are greater than the deviations calculated from the total length of line repaired in that soil (column 4). Errors in mapping the type boundaries and in locating the places where repairs were made in small bodies of soil introduce larger errors than in a single body of equal area.

The wide spread in the data summarized in table 2 may be illustrated by the repairs in a single soil type. In table 3 are shown the repairs in five bodies of the Lordstown sandy loam.

TABLE 2

Summary of data on pipe line repairs

SOIL TYPE	LENGTH OF LINE IN HUNDREDS OF FEET	PERCENTAGE OF PIPE REPAIRED	STANDARD DEVIATION OF PERCENTAGE REPAIRED σX	NUMBER OF BODIES	AVERAGE PERCENTAGE REPAIRED PER BODY	STANDARD DEVIATION OF PERCENTAGE REPAIRED PER BODY σX	STANDAR DEVIATION OF MEAN PER BODY σM
A_1	2,180	46.2	22.3	30	45.3	24.8	4.6
A_2	505	7.0	10.3	6	10.4	11.5	5.1
B	164	23.3	15.1	4	23.6	15.3	8.8
Bc_1	2,231	34.1	19.6	41	29.9	24.8	3.9
Bc_2	3,101	18.4	19.3	15	13.7	35.0	9.4
C	1,324	13.3	11.0	19	11.8	9.8	2.3
Ca	1,891	6.2	7.5	14	6.1	8.5	2.4
Ch	907	31.7	24.2	20	28.5	23.9	5.5
Ci	562	59.6	25.0	7	45.8	29.5	12.0
Cs_1	1,659	30.8	16.9	34	29.4	21.9	3.8
Cs_2	330	3.5	4.8	4	6.4	8.8	5.1
D	317	19.6	28.3	9	22.8	26.6	9.4
E	655	16.1	14.7	15	15.7	14.4	3.8
G	367	33.9	28.9	13	40.3	33.7	9.7
H	928	27.7	15.1	17	38.5	25.6	6.4
K	160	28.6	37.4	4	39.5	43.1	24.9
Kc	745	7.1	5.9	8	7.1	3.3	1.2
L	290	3.3	10.5	5	12.7	22.3	11.1
Li	680	11.1	2.7	3	11.4	2.4	1.7
Lf	184	0.0	....	2	0.0	....	....
M	5,637	20.9	13.3	27	21.7	18.6	3.6
Ms	1,671	22.8	30.6	24	26.6	31.9	6.6
Mu	134	39.4	16.2	3	25.7	21.4	15.2
N	535	57.0	....	2	79.0	....	....
Nf	207	6.5	10.7	6	6.1	10.7	4.8
P	1,160	3.1	5.1	19	3.3	4.9	1.2
S	3,555	4.0	4.2	9	3.7	4.5	1.6
T	610	20.0	20.0	21	22.6	20.9	4.7
Ti	365	26.3	23.0	11	24.5	25.7	8.1
V	4,105	13.6	14.2	35	16.4	16.0	2.7
Vl	405	7.1	3.2	4	7.2	4.3	2.5
Wf	278	12.4	8.2	4	12.5	9.1	5.3
Wl	3,715	6.0	7.7	39	11.9	14.0	2.3
W	240	6.3	....	1	6.3	....	....
Wa	640	61.0	23.1	5	51.3	24.0	12.0

It is easily seen that the repairs of 570 feet in the 1,000-foot length of pipe line are inconsistent with the fact that only 380 feet of pipe were repaired in the remaining length of 28,000 feet. At the place where the pipe was repaired,

which extended for 200 feet (5 lines) it would appear either that the soil is not really Lordstown sandy loam or the pipe did not require reconditioning solely on account of soil corrosion.

The distribution of corroded areas as related to soil type is shown graphically in figure 1 for a typical section of the lines. Pertinent data such as the total and repaired lengths of line in each area and acidity and resistivity data are also shown.

The marked differences in the corrosiveness of several soil types is immediately apparent in figure 1. In the areas occupied by the Chenango silt loam (D) and the Holly clay loam (H), it is seen that as many as three separate repairs have been made on short lengths of the lines. In contrast to these severely corrosive areas are intervening areas of Wooster loam (Wl) in which the repairs have been negligible. Similarly, it is seen that the area occupied by the Mahoning silt loam (M) is corrosive, but that few if any repairs have been made in the Canfield (Ca) and Ellsworth (E) silt loams and in the Volusia loam (Vl).

TABLE 3

Repair data for Lordstown sandy loam

LENGTH	REPAIRED LENGTH	PERCENTAGE REPAIRED
feet	*feet*	
2,000	0	0
1,000	570	57
10,500	0	0
9,500	0	0
6,000	380	6.33
Totals....29,000	950	3.27

Figure 1 further illustrates the errors, previously referred to, which may occur at the boundaries of the different soils. Thus it is seen that practically all of the repairs which have been necessary in the area of Wooster loam between 1,000 and 5,000 feet have been made at the boundaries of the adjacent soil types.

INFLUENCE OF TOTAL ACIDITY AND RESISTIVITY ON CORROSIVENESS OF SOIL TYPES

In view of the importance of soil acidity as a factor in corrosion it was anticipated at the beginning of this study that the average total acidity of the soil types could be correlated with their corrosiveness. Although such a correlation can be shown to hold for certain sections of the line where other factors such as resistivity and topography are subject to only slight variation, no worthwhile correlation between acidity and corrosion obtains for the pipe line as a whole. It can be shown, however, that if the average resistivity of the types is also considered, a fairly satisfactory correlation is obtained.

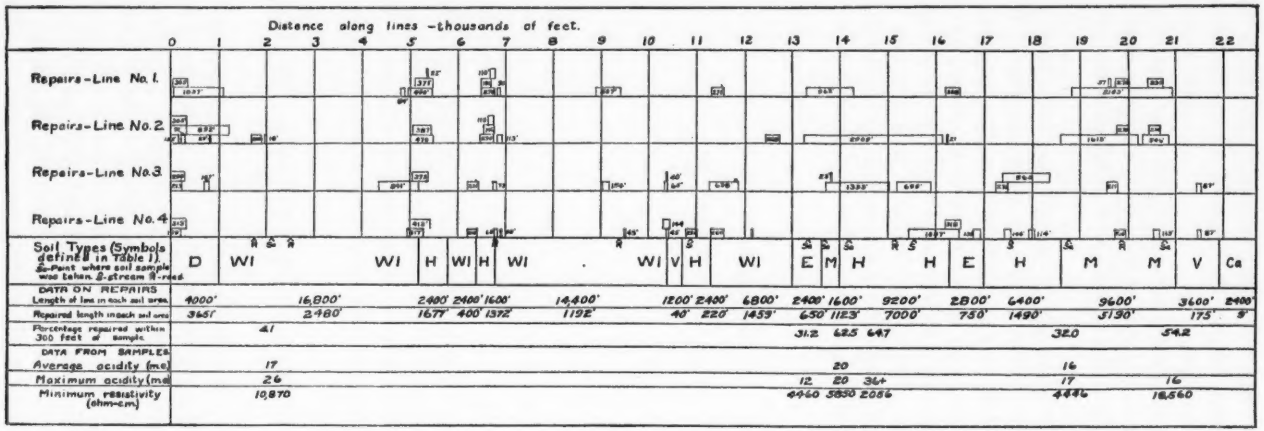
Distance along lines - thousands of feet.
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Repairs - Line No. 1.
Repairs - Line No. 2.
Repairs - Line No. 3.
Repairs - Line No. 4.
Soil Types (Symbols defined in Table I). S - Point where soil sample was taken. S - stream R - road.
D WI WI H WI H WI V H WI E M H H E H M M V Ca
DATA ON REPAIRS
Length of line in each soil area. 4000' 16,800' 2400' 2400' 1600' 14,400' 1200' 2400' 6800' 2400' 1600' 9200' 2800' 6400' 9600' 3600' 2400'
Repaired length in each soil area. 365' 2480' 1677' 400' 1312' 1192' 40' 220' 1459' 650' 1123' 7000' 750' 1490' 5190' 175' 8'
Percentage repaired within 300 feet of sample. 41 31.2 62.5 64.7 32.0 54.2
DATA FROM SAMPLES
Average acidity (me) 17 20 16
Maximum acidity (me) 24 12 20 36+ 17 16
Minimum resistivity (ohm-cm) 10,870 4460 3830 2086 4446 16,560

FIG. 1. TYPICAL SECTION OF PIPE LINES SHOWING REPAIRS AND SOIL DATA

In order to study the separate influence of acidity and resistivity on the corrosiveness of the soil types, soils of different acidities but having nearly equal resistivities were arranged in the order of increasing acidity. It was observed that the corrosiveness of such soils was roughly proportional to their acidity. Similarly, by arranging soils of approximately the same acidity in the order of decreasing resistivity, a rough inverse proportionality between corrosiveness and resistivity can be shown. These correlations are illustrated in table 4. In preparing this table the data for the Lorain fine sandy loam was omitted, the extent of the soil along the line (less than one-half mile) being too small to render the data significant.

TABLE 4

Repairs in soil types as influenced by total acidity and resistivity

TOTAL ACIDITY 15–18 M.E.			RESISTIVITY 4000–5000 OHM-CM.		
Soil type	Resistivity	Repairs	Soil type	Total acidity	Repairs
	ohm-cm.	*per cent*		*m.e.*	*per cent*
Lordstown fine sandy loam	11,450	3.3	Wauseon fine sandy loam	7.5	6.3
Wooster loam	8,002	6.0	Caneada silt loam*	12.7	13.3
Volusia silt loam	5,473	13.6	Miami silt loam†	16.8	22.8
Mahoning silt loam	4,903	20.9	Mahoning silt loam	18.1	20.9
Miami silt loam	3,982	22.8	Trumbull clay loam‡	21.1	20.0
Nappanee clay loam	1,009	57.0	Crosby silt loam, 1st section	22.0	30.8

* Includes fine sandy loam.

† Includes clay loam and fine sandy loam.

‡ Includes silt loam.

The percentage of the line repaired in the soil types investigated for the particular period may be roughly expressed in terms of the acidity and resistivity of a soil by the equation:

$$P = \frac{7{,}500\,(A - 5)}{R}$$

where P = the percentage of pipe repaired in each soil type

A = the average acidity of the soil

R = the average resistivity of the soil.

By means of this relation the corrosiveness of each soil type was calculated and the results obtained were plotted against the actual repairs made in the corresponding soils, with the results shown in figure 2.

If only those soils having a wide distribution along the pipe line are considered, it is apparent that the calculated repairs in the majority of these soils are nearly equal to the actual repairs. A possible explanation, which has been

previously given, for the failure of the calculated repairs in soils A_1 and Bc_1, to conform more exactly to the actual repairs is that cinders overlying these soils in certain areas may have increased their corrosiveness.

It will be observed in figure 2 that the flood plain and terrace soils; namely, the Braceville (B), Chagrin (Ch), Chenango (D), and Genesee (G), are much more corrosive than would be predicted from the results of the laboratory tests. Since these soils are either poorly drained or are adjacent to streams, it is reasonable to expect that electric currents, flowing along the pipe line, would dis-

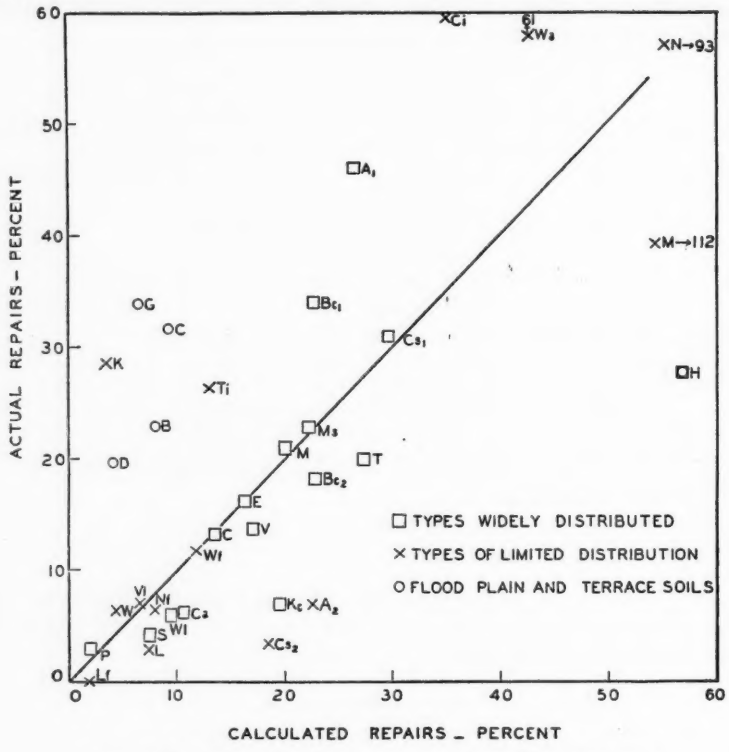

FIG. 2. RELATION BETWEEN ACTUAL AND CALCULATED REPAIRS

charge in such areas, tending thereby to accelerate the rate of corrosion. Whether current is actually discharged in these particular areas has not been determined by actual measurement, but Shepard (6) has shown that currents are discharged in areas of low electrical resistance. Since such areas frequently result from deficient drainage, the supply of oxygen at the pipe surface would necessarily be less than in better drained areas. Because of this differential aeration, it is probable that a potential difference is produced, the pipe in the wet soil being anodic and hence subject to corrosion.

COMPARISON OF CORROSIVENESS OF SOIL TYPES WITH DEGREE OF DEVELOPMENT OF THE SOIL PROFILE

In considering further the relation between the various soils and their corrosiveness, it is of interest to compare the repairs made in certain soils with the degree of development of the horizons within the soil profile. In table 5 the typical upland soils of northeastern Ohio, which have developed from sandstone and shale, have been grouped in four vertical columns according to the degree of development shown by their profiles. Within each vertical column the soils are arranged according to the texture of the B-horizon. In table 6 a similar arrangement is shown for the glacial soils of northwestern Ohio, which have been derived from limestone.

It is seen from the tables that the corrosiveness of the soils is related to their stage of development, the less well developed soils being invariably the most corrosive. Thus the Trumbull soils, which are mottled throughout the profile and show very little differentiation into horizons, are seen to be corrosive, whereas the Wooster soils, which are well developed, are non-corrosive. It will also be observed that within the vertical columns corrosiveness increases as the subsoil becomes heavier in texture.

These relations between the stage of development and texture of the soils and their corrosiveness can be largely explained on the basis of their average acidity and resistivity. Because of the slight weathering that has occurred in the case of the poorly developed soils, such as those of the Trumbull series, there has been but little tendency for soluble materials to be removed, with the result that the average resistivity of these soils is relatively low. Similarly, the very heavy texture of poorly drained soils accounts largely for their high acidity, the acidity of a soil being a function of its content of colloidal material. Conversely, the high stage of development of the non-corrosive Wooster soils has resulted from the thorough removal of soluble salts, as indicated by their high average resistivity.

Aside from the effects of acidity and resistivity, however, it is highly probable that those differences in the physical characteristics of the soils which determine their drainage and aeration have an important bearing on the observed relations.

Although it is evident that there is a wide range of variation within the soil type, and that the corrosiveness of a soil type can be only roughly predicted, the economic value of the methods described in combatting corrosion on pipe lines can be abundantly justified. If adequate protection were applied to the pipe lines considered in this study in only those soils which have been shown to be corrosive, very large savings in the annual cost of maintenance could be effected. Ewing (5) in a previous paper has estimated this saving to be 24 per cent of the annual operating cost, using reasonable values for coating and repair costs. It is of course impossible with present methods to determine the corrosiveness of soils accurately, but Ewing has shown that the savings which might be effected by using the formula which connects the repairs in each type

TABLE 5

Relation between the degree of development of the glacial soils of northeastern Ohio and their corrosiveness

	DEGREE OF DEVELOPMENT							
	1		2		3		4	
Color of surface soil	Gray		Gray brown		Light brown		Brown	
Mottling of A_2 horizon	Mottled		Mottled		No mottling		No mottling	
Mottling of B horizon	Mottled		Mottled		Mottled		No mottling	
Mottling of C horizon	Mottled		Mottled		Mottled		No mottling	
Distinguishing characteristics of B-horizon	Series	Repairs	Series	Repairs	Series	Repairs	Series	Repairs
		per cent		*per cent*		*per cent*		*per cent*
Light	.....	....	Volusia	13.6	Canfield	6.2	Wooster	6.0
Heavy	Trumbull	20.0	Medina	*	Rittman	*	.....	...
Very heavy	Trumbull	....	Mahoning	20.9	Ellsworth	16.1	.....	...

* Series not identified along pipe line.

TABLE 6

Relation between the degree of development of the glacial soils of northwestern Ohio and their corrosiveness

	DEGREE OF DEVELOPMENT							
	1		2		3		4	
Color of surface soil	Grayish black		Dark gray		Gray brown		Brown	
Color of subsoil	Mottled bluish gray		Mottled bluish gray and yellowish brown		Mottled yellowish brown and yellowish gray		Reddish brown no mottling	
Distinguishing characteristics of B-horizon	Series	Repairs	Series	Repairs	Series	Repairs	Series	Repairs
		per cent		*per cent*		*per cent*		*per cent*
Light	.....	....	.....	....	Miami	22.8	Bellefontaine	*
Heavy	Clyde	46.2	Brookston	34.1	Crosby	30.8	.....	.....
Very heavy	.....	....	Paulding	*	Nappanee	57.0	.....	.....

* Series not identified along pipe line.

with the average acidity and resistivity, may amount to about 16 per cent of the annual maintenance cost.

SUMMARY

The soils occurring along a 200-mile section of a pipe line system in Ohio have been mapped, and the corrosiveness of each type has been estimated from the corrosion actually experienced in operating the pipe lines. The average total acidity and resistivity of each of the soil types were determined and correlated with the known corrosiveness of the soils. A formula was derived whereby the corrosiveness of the soils can be approximated from the values for total acidity and resistivity. Flood plain and terrace soils are, however, more corrosive than would be indicated by the formula. The corrosiveness of the soils has been related to the texture of the subsoil and to the degree of development shown by the soil profile. Soils having the heaviest subsoils and showing the least profile development were found to be the most corrosive. Very little corrosion occurred in light-textured, well-drained soils.

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A COMPARISON OF POTASSIUM PERMANGANATE AND CERIC SULFATE FOR THE OXIDATION OF COBALTINITRITE IN THE ESTIMATION OF POTASSIUM IN KCl SOLUTION AND IN AMMONIUM ACETATE SOIL-EXTRACTS[1]

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The studies reported herein grew out of experimentation in connection with another problem in which it was desired to determine the replaceable potash in a number of field plots located on Sassafras silt loam soil. Neutral normal ammonium acetate was used to extract the soil. The extract was evaporated to dryness over a steam bath, and the organic matter was destroyed by twice adding and evaporating aqua regia over a steam bath and then removing the silica by double dehydration. The potash was then determined by means of platinic chloride according to the Official Method (1) for the determination of potash in mixed fertilizers. Since the small amount of potash in the extract necessitated the use of practically all of one leachate for a single determination, and since duplicate determinations frequently disagreed, the use of the platinic chloride method was discontinued and the sodium cobaltinitrite method tried.

Most of the workers using the sodium cobaltinitrite method, including Milne (3), Hibbard and Stout (2), and Volk and Truog (5) add an excess of potassium permanganate and a small amount of sulfuric acid to the precipitate and bring to a boil. Then an excess of either standard oxalic acid or sodium oxalate is added and titrated to a faint pink with potassium permanganate. Schueler and Thomas (4), however, titrate directly with permanganate without the uses of an oxalate solution. They claim the direct titration is much quicker and just as accurate. For that reason it was decided to try their modification of the sodium cobaltinitrite method.

PRELIMINARY EXPERIMENTS

A stock solution of KCl in water was prepared for use in some preliminary experiments so that 10 cc. of the solution would contain 5.244 mgm. of potassium. Determinations by the Schueler and Thomas method were made on a number of 10-cc. aliquots of the solution. At first the results were all low, probably because of the loss of nitrous acid during titration. Later, satisfac-

[1] Published with the permission of the director of the Delaware Agricultural Experiment Station. Contribution from the department of agronomy.

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tory results were obtained by keeping an excess of the permanganate in the upper part of the liquid while titrating until the end point was approached. It takes a little practice to learn how to do this titration. Gently stir the top of the liquid in the beaker with a glass rod, but do not stir the whole contents of the beaker until the titration is almost completed.

Five determinations were made on the stock solution using the Schueler and Thomas method up to the point of titration. At that point excess permanganate and 10 cc. of 1:1 sulfuric acid were added and brought to a boil; excess standard sodium oxalate was added and then titrated to a faint pink with permanganate. The results were essentially the same as those from direct titration with permanganate. This supports the contention that the use of an oxalate is not necessary.

Schueler and Thomas prescribe a wash solution. In several determinations ice-cold distilled water was compared with the wash solution. There was very little difference in the results: the water apparently gave slightly lower values. Probably the cold water would be satisfactory, provided the proper factor were used.

Some workers do not use alcohol in connection with the cobaltinitrite method. For that reason four determinations were made on the stock solution by the Schueler and Thomas method, except that no alcohol was added. If the factor given by those authors is used in calculating the potassium values, the results were all low. However, the potassium equivalent factor for these four determinations was calculated and found to correspond almost exactly to the one given by Volk and Truog (5), who use no alcohol in this connection. This seems to indicate that alcohol can be used or left out depending on what factor is used.

The asbestos pad recommended for filtering does not always work well. It may be too thick or too compact for rapid filtering. When the pad is thick, considerable washing may be necessary to remove the excess cobaltinitrite solution. Besides, this asbestos pulp in the titration beaker interferes to some extent in determining the exact end point. These objections to the asbestos pad led the author to try talc in a Jena fritted glass filter funnel 39 G 3.[3] This method was found more satisfactory. When the talc is properly prepared and correctly placed in the funnel the filtration is rapid, less washing is required, and the small amount of talc transferred to the titration beaker interferes less in determining the exact end point. The talc has to be thoroughly washed and the finer particles removed by decantation. A water suspension of the washed product should be prepared of such a consistency that a few cubic centimeters when poured in the fritted glass filter funnel and allowed to settle will form a talc layer somewhat thinner than 1 mm. The talc suspension should be

[3] Since this paper was submitted for publication a Jena fritted glass filter funnel 39G2 has been specially imported. In connection with the talc, it filters much more rapidly than the 39G3 funnel, and the results obtained seem to be just as reliable. Of several fritted glass filters tried, the author prefers for this particular determination the 39G2.

allowed to settle for about one-half minute, and then strong suction used to remove the surplus water. It is then ready for filtration. The talc layer should be firm and should not allow any of the precipitate to go through and collect on the fritted glass. The fact that the suspension is measured enables one to prepare a filtering surface essentially alike every time.

In removing the precipitate the funnel can be tilted to such an angle that a few cubic centimeters of cold distilled water sprayed inside the funnel will wash all of the precipitate and talc into the titration beaker. To make certain that no precipitate is left adhering to the funnel a stream of boiling water is sprayed inside the funnel and allowed to run down its side into the titration beaker. About 150 cc. of the boiling water is used for this purpose, bringing the temperature of the solution to a point where immediate titration can be made.

The fritted glass funnel after use can be quickly cleaned by drawing water through it in the opposite direction.

These preliminary experiments on the KCl solution made modifications of the Schueler and Thomas method seem unnecessary. For that reason the original method was tried on the ammonium acetate soil-extracts. The only modification ever made was that of filtration, which has been described.

DUPLICATION OF RESULTS ON AMMONIUM ACETATE SOIL-EXTRACTS

The method of extracting the soil and the procedure used in the determinations were as follows: The equivalent of 100 gm. of dry soil was leached with 750 cc. of neutral normal ammonium acetate. An aliquot was evaporated to dryness in a beaker on a steam bath, the sides of the beaker were washed down with water, 10 cc. of aqua regia was added and brought to dryness, again the sides of the beaker were washed down, and 5 cc. of aqua regia was added and brought to dryness. Then the beaker was flamed in a free flame to drive off the ammonium chloride which will adhere to the beaker. Care was taken not to get the beaker hot enough to drive off any of the potassium salts. After this, the residue of salts was brought into solution with distilled water and a few drops of HCl. From that point the Schueler and Thomas method was followed.

Repeated determinations of the potassium in ammonium acetate extracts of the same soil sample from a limed and an unlimed plat located on Sassafras silt loam were made. The repetitions were done at different times extending over a period of about two months. The results, given in table 1, indicate that on this kind of soil the method will give essentially the same result every time. Furthermore, known amounts of potassium added to the leachates were recovered by this method reasonably well. That gives an additional indication of reliability for use in this connection. The results thus obtained justified the determination, by the method described, of the potash in the ammonium acetate extract of a number of soil samples taken from field plats on Sassafras silt loam soil, the results of which will not be given here.

POSSIBLE OBJECTIONS TO POTASSIUM PERMANGANATE

Experience with these determinations indicated the possibility of two objections to potassium permanganate as used in the Schueler and Thomas method.

One is that the end point is not always sufficiently sharp. In these experiments 0.05 *N* permanganate was used, and the addition of three or four drops at the end point sometimes made little difference in color. This was particu-

TABLE 1

Results of repeated determinations, by the cobaltinitrite method, of the potassium in ammonium acetate leachates of the same Sassafras silt loam soil from block B

PLAT	LEACHATE	ALIQUOT TAKEN FOR DETERMINATION	K ADDED TO ALIQUOT	K FOUND	ADDED K RECOVERED	K PER 100 GM. DRY SOIL	AVERAGE
		cc.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
4 unlimed	Diluted to 1,000 cc. with H_2O	200		0.85		4.25	4.18
		200		0.82		4.10	
4 unlimed	Diluted to 1,000 cc. with H_2O	200		0.82		4.10	4.00
		200		0.78		3.90	
4 unlimed	Not diluted	200		1.27		4.36	4.21
		200		1.18		4.05	
		200	5.24	6.19	4.96		
4 unlimed	Not diluted	200		1.12		3.79	3.99
		200		1.24		4.19	
		200	5.24	6.25	5.07		
4 limed	Not diluted	275		2.00		4.28	4.28
4 limed	Not diluted	275		1.99		4.28	4.28
4 limed	Not diluted	200		1.33		4.57	4.36
		200		1.21		4.16	
		200	5.24	6.33	5.06		
4 limed	Not diluted	200		1.27		4.34	4.29
		200		1.24		4.24	
		200	5.24	6.51	5.25		

larly true in the presence of the asbestos pad. The talc did not seem to interfere as much as the asbestos.

In order to prevent the loss of nitrous acid during titration it is desirable to keep an excess of permanganate in the upper part of the liquid in the titration beaker until the end point is almost reached. The second objection is that in attempting to keep this excess one sometimes runs past the end point.

These considerations suggested the use of some other substance to oxidize

the cobaltinitrite. The fact that ceric sulfate is known to be a good oxidizing agent, and that Professor C. C. Lynch, Chemistry Department of the University of Delaware, has been using it in some of his work on potash determinations, led to its trial in this connection.

PRELIMINARY TESTS AND CERIC SULFATE METHOD

A 0.05 *N* solution of ceric sulfate was prepared and standardized. After the solution had stood in the laboratory in an ordinary glass-stoppered bottle for three months the standardization was repeated and found to be the same as at first. This indicates that the solution is very stable.

Ferrous ammonium sulfate, with ortho-phenanthroline ferrous complex as an indicator, was selected for titrating excess ceric sulfate. A trial of the titration was made with solutions at room temperature. The end point was very sharp. Less than one drop of a 0.05 *N* solution will give a change in color from a pale blue to a deep orange-red. The color contrast is so great that the author was able to titrate at night without special lights. Repeated trials always gave the same result.

The titration was repeated with hot solutions, but the results were not so good. The indicator does not appear to be very stable in hot solutions.

The preliminary tests led to the adoptation of the same procedure for ceric sulfate as that used in connection with permanganate up to the point where the hot solution is in the titration beaker. At that point an excess of ceric sulfate is run down the side of the beaker by means of a pipette, the solution stirred, 10 cc. of 1:1 H_2SO_4 added in the same manner, the solution again stirred, and the beaker put in a pan of water to cool. After the solution has reached room temperature the excess ceric sulfate is titrated with ferrous ammonium sulfate, one drop of ortho-phenanthroline ferrous complex being used as an indicator.

POTASSIUM EQUIVALENT FACTORS FOR PERMANGANATE AND CERIC SULFATE

Potassium determinations by the Schueler and Thomas and by the ceric sulfate methods were made on 10-cc. aliquots of the stock KCl solution already described. They were done at different times over a period of about a month. In all, seventeen determinations were made with potassium permanganate and sixteen with ceric sulfate. The results were used to calculate the potassium equivalent of 1 cc. of 0.1 *N* solution. The average for the permanganate determinations was 0.0005553 gm. of potassium. The largest factor for the individual determinations was 0.0005834 gm. of potassium, and the smallest, 0.0005406. Most of them were very near the average. For the ceric sulfate determinations the average was 0.0005616, the largest was 0.0005797, and the smallest was 0.0005497 gm. of potassium. Thus it can be seen that the potassium equivalent factor for ceric sulfate is essentially the same as that for potassium permanganate and the ones obtained here are very close to 0.0005672, the factor given by Schueler and Thomas.

COMPARISONS ON SOIL EXTRACTS

As already indicated, the potassium permanganate method seems to be very reliable for the determination of potassium in the ammonium acetate extract of Sassafras silt loam soil. In order to compare the potassium permanganate and ceric sulfate methods on the same soil extract, another sample of Sassafras silt loam was obtained and leached as before. Four aliquots of the leachate were taken. On two of the aliquots potassium determinations were made by

TABLE 2

Comparison of potassium determinations on the same ammonium acetate leachate of sassafras silt loam soil

150-cc. aliquot taken for each determination

NUMBER	METHOD USED	K FOUND	K PER 100 GM. SOIL
		mgm.	*mgm.*
1	$KMnO_4$	0.79	3.54
2	$KMnO_4$	0.76	3.41
3	Ceric sulfate	0.77	3.46
4	Ceric sulfate	0.77	3.46

TABLE 3

Comparison of potassium determinations on the same ammonium acetate leachate of Chester loam soil

150-cc. aliquot taken for each determination

SAMPLE	TREATMENT OF SAMPLE BEFORE LEACHING	DETERMINATION	METHOD	K IN ALIQUOT	K PER 94 GM. SOIL
				mgm.	*mgm.*
1		1	Ceric sulfate	3.79	17.18
		2	Ceric sulfate	3.74	16.93
		3	$KMnO_4$	3.71	16.80
		4	$KMnO_4$	3.71	16.80
2	10.488 mgm. K added	1	Ceric sulfate	5.97	26.60
		2	Ceric sulfate	5.89	27.22
		3	$KMnO_4$	5.95	27.48
		4	$KMnO_4$	5.95	27.48

the potassium permanganate method as previously used on this soil. On the other two, the procedure used in connection with the potassium permanganate method was followed up to the point of titration. From that point on the procedure given for the ceric sulfate method was followed. The results are given in table 2. An examination of the data indicates that the two methods of procedure give practically the same results.

The two methods were also compared on Chester loam soil. Samples equivalent to 94 gm. of dry soil were taken. One sample was leached in the way

already described. To another sample 20 cc. of KCl solution containing 10.488 mgm. of potassium was added, and then the soil was immediately leached in the regular way. Potassium was determined by the two methods. The results are given in table 3. Again the results by the two methods are very similar.

It was desired to compare further the two methods on a very sandy soil. Norfolk sand, which is known to be very low in replaceable potassium, was selected. To obviate the taking of a small aliquot in making a number of determinations on the same leachate, 225 gm. of air-dried soil was leached with 1,688 cc. of the neutral normal ammonium acetate. The proportion of soil to the acetate is the same as that used in the other leachings. Potassium determinations were made by the two methods, and the results are given in table 4.

TABLE 4

Comparison of potassium determinations on the same ammonium acetate leachate of Norfolk sand

200-cc. aliquot taken for each determination

DETERMINATION	METHOD	K ADDED TO ALIQUOT	K FOUND	ADDED K RECOVERED	K PER 100 GM. SOIL
		mgm.	*mgm.*	*mgm.*	*mgm.*
1	$KMnO_4$		0.52		1.85
2	$KMnO_4$		0.49		1.74
3	Ceric sulfate		0.50		1.77
4	Ceric sulfate		0.52		1.86
5	$KMnO_4$	5.24	5.92	5.41	
6	$KMnO_4$	5.24	5.92	5.41	
7	Ceric sulfate	5.24	6.01	5.50	
8	Ceric sulfate	5.24	5.96	5.45	

The determinations on Norfolk sand by the two methods agree almost perfectly. Potassium added to the leachate was recovered, with a slight excess, approximately 0.2 mgm., by both methods. In dealing with such small amounts of potassium some error is to be expected.

DISCUSSION

Tests made on the ammonium acetate extracts of Sassafras silt loam, Chester loam, and Norfolk sand indicate that ceric sulfate in connection with sodium cobaltinitrite can be used for the determination of potassium in that extract with about the same degree of accuracy as with potassium permanganate. Schueler and Thomas claim that their method is most accurate when determining amounts of potassium between 3 and 10 mgm. Sassafras silt loam and Norfolk sand are so low in replaceable potassium that it was not possible to repeat as often as desired the determinations on the same leachate and take an aliquot sufficiently large to be in the aforementioned range. Nevertheless, on the basis of the recovery of known amounts of potassium added to some of the aliquots, the determinations on those two soils are thought to be reasonably

accurate. Chester loam contains much more replaceable potassium, and the aliquots were within the prescribed range.

The end point with ceric sulfate, when othro-phenanthroline ferrous complex is used as an indicator, is sharper with a greater contrast of color than the end point with permanganate. However, factors other than the end point apparently limit the accuracy of the methods because the sharper end point of the ceric sulfate made no appreciable difference in the results. Nevertheless, if the other limiting factors could be removed the sharp end point of the ceric sulfate would be an advantage. The author prefers to deal with a sharp end point with contrasting colors even though the results are the same.

The Schueler and Thomas method, where the titration is made directly with potassium permanganate, may be more rapid than the ceric sulfate method. The author is not certain that such is the case, however, because a standardized pipette can be used to put the excess ceric sulfate into the titration beaker, and this takes little time. Then the only titration which has to be done is the excess ceric sulfate with ferrous ammonium sulfate. Waiting for the solutions to cool before titration involves no loss of time because a number of determinations are most frequently done at the same time. Some can be prepared while others are cooling. In titrating directly with permanganate, in his efforts to keep an excess of permanganate in the titration beaker till the end point is approached one may occasionally go beyond the end point, which is never the case in the ceric sulfate method. Because of that fact, the ceric sulfate method, even though it might be a little less rapid, is perhaps preferable to the Schueler and Thomas method.

In those methods which require two titrations with permanganate and one with an oxalate it seems to the author that the use of the ceric sulfate in place of the potassium permanganate should have considerable advantages.

SUMMARY AND CONCLUSIONS

Preliminary experiments in connection with the Schueler and Thomas method indicated that there is a possibility of using ice-cold distilled water for the wash solution. Alcohol may not be necessary. Talc with a fritted glass funnel seemed to be better for filtration than an asbestos pad.

The Schueler and Thomas method is reliable for the determination of potassium in the ammonium acetate leachate of Sassafras silt loam soil, if duplication of results and the recovery of potassium added to the leachate are considered measures of reliability.

A procedure for the determination of potassium by means of ceric sulfate is given.

A comparison between seventeen determinations of potassium in a KCl solutions by means of potassium permanganate and sixteen determinations on the same solution by means of ceric sulfate was made. The potassium equivalent factors were essentially the same.

The ammonium acetate extracts of Sassafras silt loam, Chester loam, and

Norfolk sand were analyzed for potassium by both methods. There was close agreement in all cases. Known amounts of potassium added to some of the leachates were recovered reasonably well, indicating that both methods are reliable for the determination of small amounts of potassium in these soil extracts.

In some respects ceric sulfate seems to be preferable to potassium permanganate for potassium determinations.

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ORGANIC SOIL CARBON BY REDUCTION OF CHROMIC ACID[1]

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A study of the organic carbon content of soils involves two pertinent considerations; namely, representative sampling and the use of suitable analytical methods. It is recognized that, because of the non-uniform nature of soils even within short distances, sampling errors usually exceed analytical errors. Soil carbon is no exception. In order to reduce the sampling error equal to, or below, the error of analysis a larger number of individual borings is necessary than is ordinarily taken. With 20 borings per twentieth-acre plot, a difference of from 3 to 5 per cent between duplicate samples frequently occurs, which is reduced only very slightly by further increase in the number of borings per plot. There is little justification, therefore, for attaining, at the expense of much time, a degree of accuracy in analysis far in excess of that which is attained in sampling.

Two methods are commonly used for carbon determinations, both of which offer certain disadvantages. Wet combustion (4, 10) is time-consuming and, moreover, is subject to the danger involved in handling boiling sulfuric acid. Standard furnace combustion (11) (combustion in a tube furnace with current of oxygen, purifying train, and absorbant in bulb for gravimetric estimation of CO_2) is more accurate than the former for determining total soil carbon, but it is also slow and requires expensive apparatus. This method does not distinguish between organic- and carbonate-carbon and is subject to the additional objection, particularly where agronomic interpretations are involved, of determining inert carbon, derived from cinders, fragments of coal, or carbonized soil organic matter. From the standpoint of soil productivity this inert carbonaceous matter does not function in the same manner as organic matter derived from decaying vegetation.

Recently Anderson and Byers (1) pointed out the need for a method capable of "distinguishing between charcoal and coal fragments and soil organic matter." An experience of the writer bears upon this question. In checking Schollenberger's chromic acid reduction method (5, 6) against standard furnace combustion (11) on some laboratory stock samples, widely divergent carbon

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values were obtained for sample 14043. Furnace combustion gave values 21 per cent higher than the reduction method (table 1). After the analysis was repeated with similar results the source of the sample was investigated. This sample was obtained within a few feet of a railroad right-of-way and, upon physical analysis, revealed the presence of fragments of cinders and incompletely burned coal. Sample 14052 taken 200 feet farther from the railroad was cinder-free, and its carbon value showed good agreement by the two methods. These data suggest that the chromic acid reduction procedure, by failing to determine relatively inert carbon, gives data more nearly representing the organic carbon of the soil than does the furnace combustion method.

Since both the wet and dry combustion methods for determining organic carbon have objectionable features, the writer directed his attention to Schollenberger's chromic acid reduction method (5, 6). In addition to being rapid, it requires only simple apparatus. This paper reports a study of the value of the method for the determination of soil organic carbon.

TABLE 1

Effect of inert carbon on percentage of total soil carbon by two different methods

SAMPLE*	LOCATION	INERT CARBON	CARBON	
			Furnace combustion	Chromic acid reduction
			per cent	*per cent*
14043	Near railroad	Cinders	2.36	1.95
14052	200 feet from railroad	None	2.27	2.24

* Samples from S. W. 1/4 of Sec. 15, T. 15 N., R. 6 W. of 3rd P. M. in Sangamon County, Illinois.

The method, in brief, consists in the oxidation of a sample in concentrated sulfuric acid containing excess potassium dichromate, by heating to 175°C. in 90 seconds, cooling, and titrating the *unused* chromic acid with a standard solution of 0.2 *N* ferrous ammonium sulfate, using diphenylamine as internal indicator.

EXPERIMENTAL

As stated by Schollenberger (5), 1 ml. of 0.2 *N* ferrous ammonium sulfate is equivalent to 0.009807 gm. of potassium dichromate or 0.0006 gm. of carbon. Based on a uniform sample of 0.5000 gm. and 100 per cent recovery, the theoretical factor for carbon is, then: $0.0006 \times 100/0.5 = 0.12$ per cent for each milliliter of ferrous ammonium sulfate. By the use of this value with furnace combustion as a standard of comparison, the percentage recovery on five 100-mesh, carbonate-free samples, representing surface and subsoil as well as different soil types, was found to vary between 86.1 and 87.8 per cent, averaging 86.9 per cent (column 5, table 2). These results indicate a uniformly incomplete oxidation of organic carbon. A conversion factor equivalent to 100 per

cent recovery of carbon was obtained as follows: 100 / 86.9 = 1.15. By combining this with the theoretical factor as modified for a 0.5 gm. sample, a single factor is obtained for computation: thus, 1 ml. of ferrous ammonium sulfate = 1.15 × 0.12 = 0.138 per cent organic carbon. Further evidence of the correctness of this factor is presented later.

Nearly all investigators reporting the use of Schollenberger's method have recommended modifications. In these modifications, however, either the accuracy of the method or the rapidity of its operation has been impaired.

Degtjareff (3) advised the addition of 10–15 ml. of 0.3 per cent H_2O_2 to the sample followed by a 1.6 per cent chromic acid solution in concentrated H_2SO_4.

TABLE 2

Calibration of Schollenberger's chromic acid reduction method against soils of known carbon content

Air-dry basis

SAMPLE NUMBER	CARBON BY FURNACE COMBUSTION	CARBON USING THEORETICAL FACTOR: 1 ML. 0.2 *N* Fe^{++} SOLUTION = 0.12 PER CENT CARBON		CARBON RECOVERY	CARBON USING CALCULATED FACTOR: 1 ML. 0.2 *N* Fe^{++} SOLUTION = 0.138 PER CENT CARBON
	per cent	*per cent*	*Average*	*per cent*	*per cent*
3 777	4.11	3.60			
		3.62	3.61	87.84	4.15
3 780	1.66	1.43			
		1.45	1.44	86.75	1.65
K 301	3.31	2.86			
		2.84	2.85	86.11	3.28
K 308	4.01	3.48			
		3.50	3.49	87.04	4.01
K 309	3.92	3.39			
		3.42	3.40	86.74	3.91
Average				86.90	

He applied no external heat because the heat of solution of $H_2SO_4+H_2O_2$ was considered sufficient to oxidize the sample. All subsequent steps were the same as in the original procedure. The writer found the method inconsistent. A similar finding has recently been reported by Walkley and Black (9). They studied Degtjareff's method in detail including the interaction of H_2O_2 and chromic acid and found that "the procedure is without a sound theoretical basis for its action."

Tiurin (8), who likewise condemned Degtjareff's procedure, recommends boiling the sample for 5 minutes in a solution of chromic acid in 1:1 sulfuric acid and water. In checking this method good agreement was obtained with

Schollenberger's method where the boiling was controlled with a flame. When a hot plate was used the controls failed to boil, but rather evaporated slowly with a rise in temperature, giving low titrations and incurring a considerable error. This method gave no higher recovery of organic carbon and since it requires 5 minutes boiling as contrasted to heating for only 1.5 minutes, it seems to offer no advantage over the original method.

Following their study of the Degtjareff method, Walkley and Black (9) recommended that the method be simplified by adding the chromic acid in aqueous solution to the sample followed by the addition of 20 ml. of concentrated H_2SO_4, allowing the heat of solution of water and acid to replace the application of external heat. After being shaken one minute the sample is cooled and titrated in the usual way. This method was found by the writer to give a maximum temperature of 124°C., which is not sufficiently high to recover a definite fraction of organic carbon present in different soils. The percentage recovery reported by Walkley and Black ranged from 60 to 86 per cent.

Following is Schollenberger's method in detail as used in the work reported in this paper. Experience with the method has led the writer to make a few minor changes, which are reported because they offer what seems to be a simplification of the technic, giving some increase in rapidity without sacrificing accuracy.

Reagents:

1. Potassium dichromate, C.P., pulverized and dried.
2. Fifth-normal ferrous ammonium sulfate. Dissolve 78.6 gm. of C.P. crystals in distilled water containing 20 ml. of H_2SO_4 and make up to 1 liter. This reagent may be prepared in larger quantities and stored under hydrogen supplied by a Kipp generator. Since deterioration is very slow under hydrogen, controls need be run only every week or 10 days.
3. Indicators:
   a. Diphenylamine—Dissolve 0.5 gm. in 100 ml. of conc. H_2SO_4; pour carefully into 20 ml. cold water.
   b. Alternate indicators:
      Ortho-phenanthroline.
      Barium diphenylamine sulfonate.

Procedure: Weigh 0.1961 gm. potassium dichromate and place in a 150 x 25 mm. Pyrex test tube. In order to save the time of individual weighings of the dichromate, add a 10-ml. portion, using a standardized pipette, to each tube from a solution prepared by dissolving 19.61 gm. of the salt in 1 liter of distilled water. Place tubes in wire basket or racks and take down to dryness overnight in an oven at 80–85°C. Avoid higher temperatures to prevent spattering.

Weigh 0.5000 gm. soil and transfer into tube. Add 10 ml. of conc. sulfuric acid from a burette so as to wash down wall of tube.

Place tube in ring stand fitted with a suitable clamp. Heat steadily over a low flame (2–3 cm. high), while stirring constantly to the bottom of the tube

with a 350° thermometer, so that a temperature of 175°C. is attained in about 90 seconds. Avoid heating above 180° and also avoid heating too rapidly, which causes excessive fuming of acid. Careful attention to these points is essential to success with the method.

Allow tube to cool 5 minutes in air and then in running tap water until thoroughly cooled. Pour contents of tube into 50 ml. of cool distilled water in 250-ml. beaker and rinse tube several times or until total volume is about 150 ml. Add about 5 gm. sodium fluoride—a level teaspoonful.

Titrate with 0.2 *N* ferrous ammonium sulfate. With 3 drops of diphenylamine the color change is from blue to green, giving a slow but distinct transition at the end point. Ortho-phenanthroline and barium diphenylamine sulfonate (7) give instantaneous changes from pale blue to red and from blue to green, respectively, and for that reason offer some advantage over diphenylamine.

Deduct the burette reading from that of a blank determination made under exactly similar conditions, except that no sample is used. If 0.2 *N* ferrous ammonium sulfate is used, the blank titration, against 0.1961 gm. of potassium dichromate, should be exactly 20 ml. In case the solution is more, or less, than 0.2 *N* the corresponding organic carbon factor may be obtained by substituting the blank titration in the following equation:

$$\frac{20.00}{\text{ml. blank} \times 0.138} = \text{new factor}$$

In comparative studies with this method best results were obtained where a uniform weight of sample (0.5000 gm.) was used. For soils of 2.5 per cent or more of organic carbon it is preferable to use one and one-half or two times the previously designated weight (.1961 gm.) of dichromate rather than to reduce the sample below 0.5000 gm. A moderate excess of dichromate is essential, otherwise a considerable error may occur. As soon as properly cooled, the oxidized samples should be diluted to the required concentration, after which they may be permitted to stand. This permits 10 or more oxidations and subsequent titrations in a single group.

Since the quantity of soil actually used is small, carefully prepared, 100-mesh samples should be used, although for roughly quantitative work whole, unground samples serve satisfactorily. Pulverizing in an iron mill is satisfactory for all soils except those containing considerable sand. In the case of the latter, sufficient iron may be ground off the mill plates to cause appreciable errors, since iron acts to some extent as a reducing agent. For normal agricultural soils, however, this factor is negligible provided the samples are screened free of pebbles or coarser particles.

Since the reduction method has been calibrated against a relatively small number of samples it seemed desirable to subject it to a more extensive test. Fifteen laboratory stock samples[3] of known carbon content by furnace com-

[3] These samples were supplied by Mr. Eric Winters, Jr., of the Division of Soil Physics, who made the chemical analysis by the furnace combustion method (11), the data for which are reported in table 3.

bustion were used. They represent different horizons from four common soil types occurring in Illinois and provide a wide range in carbon content. The analysis of these samples (table 3) indicates that the reduction procedure gives consistent recovery of carbon in all horizons regardless of amounts present. In other words, the organic matter in the different horizons is attacked to the same degree under the conditions of the method.

A study of organic matter accumulation on certain of the outlying soil experiment fields of the Illinois Experiment Station, in progress at the time the method was being studied, offered an opportunity to compare the errors

TABLE 3

A comparison of Schollenberger's chromic acid reduction method for organic soil carbon with furnace combustion

Dark-colored soils

NUMBER	TYPE	HORIZON	DEPTH	CARBON	
				Furnace combustion	Chromic acid reduction*
			inches	*per cent*	*per cent*
13 777	Muscatine silt loam	A_1	0–8	4.11	4.18
13 780	Muscatine silt loam	B_1	18–25	1.66	1.69
14 052	Muscatine silt loam	A_1	0–8	2.27	2.24
14 034	Muscatine silt loam	A_1	0–6	2.53	2.49
14 035	Muscatine silt loam	A_2	8–14	1.46	1.46
14 036	Muscatine silt loam	B_1	14–18	0.86	0.87
13 873	Grundy silt loam	A_1	0–6	3.13	3.18
13 876	Grundy silt loam	A_4	14–17	1.98	1.98
13 878	Grundy silt loam	B_2	23–27	0.70	0.69
13 915	Tama silt loam	A_1	0–6	2.38	2.38
13 918	Tama silt loam	B_1	13–18	1.11	1.08
13 920	Tama silt loam	B_3	29–35	0.42	0.42
14 075	Putnam silt loam	A_1	0–6	2.35	2.43
14 076	Putnam silt loam	A_2	6–12	1.22	1.20
14 078	Putnam silt loam	B_1	16–22	0.68	0.63

* Using new factor: 1 ml. 0.2 *N* ferrous ammonium sulfate = 0.138 per cent organic carbon.

involved in sampling with those of analysis, using furnace combustion (11) as the standard of reference.

Fourteen unlimed twentieth-acre plots from the Raleigh field and a similar number from the Ewing field were sampled by taking 20 borings to a depth of 7 inches, according to the following plan:

a	b	a	b	a	b	a	b	a	b
b	a	b	a	b	a	b	a	b	a
a	b	a	b	a	b	a	b	a	b
b	a	b	a	b	a	b	a	b	a

The "a" borings and the "b" borings were composited separately to make the duplicate samples. Thus from each field 14 duplicate samples were obtained. The samples were air-dried and were passed through a Braun pulverizer and then through a 100-mesh sieve.

DISCUSSION OF RESULTS

The carbon values for the duplicate samples obtained from the Raleigh and the Ewing fields are given in table 4. An interpretation of these data is given in table 5 in such a manner as to afford a comparison of the errors of sampling and those due to the two different methods of analysis used in this study.

Standard deviations, by Students' method (2), were computed by considering differences between duplicate soil samples as deviations of the carbon value of duplicate "b" from that of duplicate "a", the latter serving as the base for comparison. In a similar way differences between the two chemical methods are reported as deviation of the carbon value by chromic acid reduction from that by furnace combustion, where the latter serves as the base for comparison. Since standard deviations alone do not give direct information concerning either the magnitude or the frequency of occurrence of the individual deviations, for methods of analysis or of sampling, these facts are presented in table 5, along with standard deviations.

The outstanding fact indicated by the data in table 5 is that the variation between chromic acid reduction and furnace combustion (S.D. = 1.18–1.24) is significantly less than the variation between duplicate samples by either method of analysis (S.D. = 1.50 for combustion and 1.90 for reduction). This point is borne out also by the fact that the reduction values deviate from the combustion values by 2 per cent or more of the carbon in the sample in only three instances out of a total of 56, whereas, the "b" sample values deviate from the "a" sample values by the same amount or more in 9 instances out of 28 where the analysis was made by chromic acid reduction, and in 5 instances out of 28 where furnace combustion was used. This analysis reveals that the initial and by far the greatest error, in a comparative study of this nature, is made at the time the samples are taken.

It was mentioned earlier in this paper that, as pointed out by Anderson and Byers (1), there has been no satisfactory method for detecting the presence in soils of small quantities of relatively inert (non-organic) carbon such as charcoal and cinders. The results of this study indicate that such inert forms of carbon may be estimated as the difference between total carbon by furnace combustion and organic carbon by chromic acid reduction, provided the amounts present are in excess of the experimental error inherent in the two methods.

The consistency of performance of the reduction method is shown by the fact that, on the average, duplicate determinations checked within 0.89 per cent, whereas in the case of furnace combustion the difference between duplicates averaged 1.20 per cent of the carbon present. This fact, combined with

its close agreement with the admittedly more accurate furnace combustion method, indicates that Schollenberger's chromic acid reduction method is satisfactory for the determination of organic carbon in soil.

TABLE 4

A comparison of Schollenberger's chromic acid reduction method for organic soil carbon with furnace combustion

Light-colored soils

RALEIGH FIELD			EWING FIELD		
Sample number	Carbon		Sample number	Carbon	
	Furnace combustion	Chromic acid reduction*		Furnace combustion	Chromic acid reduction*
	per cent	*per cent*		*per cent*	*per cent*
9393a	1.34	1.35	9422a	1.16	1.17
9393b	1.34	1.36	9422b	1.14	1.13
9394a	1.29	1.29	9423a	1.23	1.25
9394b	1.27	1.27	9423b	1.22	1.23
9397a	1.41	1.43	9426a	1.05	1.06
9397b	1.40	1.41	9426b	1.07	1.08
9398a	1.47	1.47	9427a	1.03	1.02
9398b	1.44	1.46	9427b	1.03	1.05
9402a	1.22	1.26	9431a	1.07	1.06
9402b	1.22	1.23	9431b	1.09	1.08
9404a	1.04	1.05	9432a	1.03	1.05
9404b	1.02	1.03	9432b	1.03	1.02
9405a	1.15	1.16	9433a	1.05	1.06
9405b	1.17	1.15	9433b	1.09	1.09
9409a	1.15	1.14	9437a	0.79	0.80
9409b	1.13	1.14	9437b	0.78	0.81
9410a	0.93	0.92	9438a	1.00	1.01
9410b	0.91	0.89	9438b	1.01	1.02
9411a	1.00	0.99	9439a	1.06	1.06
9411b	1.00	0.99	9439b	1.06	1.07
9415a	1.16	1.17	9443a	1.21	1.19
9415b	1.13	1.13	9443b	1.21	1.21
9416a	1.00	1.00	9444a	0.91	0.92
9416b	1.02	1.02	9444b	0.92	0.92
9417a	1.03	1.02	9445a	1.04	1.06
9417b	1.02	1.00	9445b	1.04	1.04
9421a	1.17	1.16	9449a	1.25	1.26
9421b	1.18	1.16	9449b	1.24	1.23

* Using new factor: 1 ml. 0.2 *N* titrant = 0.138 per cent organic carbon.

As a final check on the correctness of the empirical factor (1.15) for converting the theoretical value of milliliters of titrant used to percentage of carbon,

all of the 76 wet combustion values from tables 2, 3, and 4 were calculated as percentage of their corresponding dry combustion values. An average of 99.97 per cent was obtained which corresponds to essentially the same factor; namely, 1.1497.

Two samples per hour was found to be the maximum rate of analysis by furnace combustion, whereas at least three samples per hour can be determined with comparative ease by the chromic acid reduction procedure as outlined. Since the latter is a reduction method, it is unaffected by the presence of carbonates, a point which gives it considerable advantage over those methods that measure evolved carbon dioxide.

TABLE 5

Analysis of data in table 4

Comparison of analytical methods

SOURCE OF SAMPLE	NUMBER OF SAMPLES	NUMBER OF CASES IN WHICH DEVIATION OF CARBON VALUES BY REDUCTION METHOD FROM THOSE BY FURNACE COMBUSTION WAS—			STANDARD DEVIATION
		<2 per cent	2–3 per cent	>3 per cent	Per cent of combustion value
Raleigh field	28	26	1	1	1.24
Ewing field	28	27	0	1	1.18

Comparison of "a" and "b" samples

ANALYTICAL METHOD	NUMBER OF SAMPLES	NUMBER OF CASES IN WHICH CARBON IN "b" SAMPLE DIFFERS FROM THAT IN "a" SAMPLE BY—			STANDARD DEVIATION
		<2 per cent	2–3 per cent	>3 per cent	Per cent of "a" value
Chromic acid reduction	28	19	6	3	1.90
Furnace combustion	28	23	4	1	1.50

SUMMARY

A critical examination of Schollenberger's method for determining soil organic carbon by the reduction of chromic acid is reported. Modifications of this procedure by other investigators have been found less desirable than the original, since they have impaired one or more of its desirable features; namely, simplicity, rapidity, or accuracy.

Compared to furnace combustion, Schollenberger's method offers the following advantages: (a) it is approximately 50 per cent more rapid, (b) it is unaffected by the presence of carbonates in the sample, and (c) it does not determine inert carbon.

The conditions of time and temperature of oxidation by chromic acid reduction give uniformly incomplete oxidation of soil organic carbon. A conversion factor of 1.15 is required to bring carbon values by this method into agreement with furnace combustion data.

The analytical error of the reduction method, although slightly greater than that of the furnace combustion method, is shown to be less than the error in a commonly accepted method of sampling; hence the accuracy of this method is adequate for the purpose intended.

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THE CHEMICAL AND BIOLOGICAL NATURE OF CERTAIN FOREST SOILS[1]

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Some of the great forests of the world are in the Pacific Northwest. Although the soils producing these forests have been little studied, it would seem that soil science may here render a service to forestry comparable to what it has rendered agriculture. Forest litter protects soil from erosion, increases absorption, and conserves water supply. It also is the parent material of underlying organic layers and, as such, largely determines the course of decompositions yielding humus and plant nutrients.

Although scientific investigation of forest soils has in the past been carried on mainly by the Forest Experiment Stations of northern Europe, several American investigators have recently made contributions to this field. It is now recognized that the different forest floors yielded by hardwood, coniferous, and mixed stands of timber with their accompanying ground covers, favor different types of decomposition and nitrogen transformation. Forest nutrition and development are thus directly influenced, and a study of the various factors concerned should be of value in forest maintenance, forest development, and the transformation of forest to agricultural land.

In a previous report by Powers (4) on the characteristics of nine northwestern forest soil profiles, evidence was presented that the fermenting and humified layers are of chief importance in supplying nutrients to forest growths. Herein is reported a study of the chemical and microbiological characteristics of two Pennsylvania and two western Oregon forest soil profiles. The Oregon soils have been further employed during the past biennium in forest nursery and greenhouse fertilizer experiments in which the nitrogen economy in these forest soils has been given special attention.

SOME CHEMICAL CHARACTERISTICS OF PENNSYLVANIA AND WESTERN OREGON FOREST SOILS

Profile samples of DeKalb and Upshaw soil series from Pennsylvania[2] and of Olympic and Aiken soil series from the Peavy Arboretum of Oregon State

[1] Published as technical paper 233 with the approval of the director, as a contribution from the Oregon Agricultural Experiment Station.

[2] The Pennsylvania forest soil profile samples were collected by Professor T. J. Starker, of School of Forestry, Oregon State College, while doing graduate work at Pennsylvania State College, and by Mr. Walter U. Garstka, instructor in the School of Forestry at Pennsylvania State College.

TABLE 1

Fertility in four forest soils

	pH	ORG. M.*	TOT. N†	BASE EXCH. CAP. MGM. PER 100 GM.
Pennsylvania forest soils				
		per cent	*per cent*	
DeKalb				
Litter	4.00	94.3	0.6125	10.6
"F" layer	4.71	90.6	1.3020	10.6
"H" layer	4.48	78.0	1.5029	10.8
A ("HS") layer	4.48	3.22	0.0690	8.9
A_2	4.12	1.05	0.0182	2.6
B_1	3.96	1.68	0.0988	12.2
B_2	4.56	1.51	0.0714	3.6
B_3	4.63	0.50	0.0406	1.7
C	4.55	0.50	.....	3.6
Upshaw:				
Litter	....	95.8	0.8540	10.3
"F" layer	....	63.1	1.0052	27.1
"H" layer	5.07	7.68	0.3066	35.5
B_1	5.68	6.46	0.2330	14.9
B_2	5.68	1.77	0.0518	14.4
C	5.22	1.55	0.0389	13.5
West Oregon forest soils				
Aiken (Peavy Arboretum):				
Litter	5.56	79.74	0.9030	27.4
"F" layer	6.06	78.31	1.0710	33.7
"H" layer	4.55	67.05	1.1200	42.1
A_1	5.39	35.44	0.6440	19.5
A_2	5.62	5.18	0.1848	12.0
B	5.52	2.86	0.1120	17.1
C	5.39	1.53	0.0364	13.9
Olympic (Peavy Arboretum):				
Litter	6.49	84.68	0.8470	24.2
"F" layer	6.15	63.50	1.1340	40.8
"H" layer	6.61	59.56	0.7630	33.3
A_1	6.38	13.28	0.3858	25.1
A	6.66	4.14	0.1596	18.4
B	6.00	1.91	0.0630	16.6
C	5.56	1.29	0.0196	18.5

* Organic matter determinations were made by the modified J. B. Rather method (*Ark. Agr. Exp. Sta. Bul.* 140, 1907) as adapted by L. T. Alexander and H. G. Byers (*U. S. Dept. Agr. Tech. Bul.* 317, 1932).

† Determined by E. F. Torgerson.

College subjected to partial chemical analyses (table 1) show that the organic matter extends deeper in the western Oregon profiles and that nitrogen extends down with it. The maximum nitrogen content in the soil profiles is found

approximately at the boundary zone of the fermenting (F) and humified (H) layers. Base exchange capacity is also maximum at about this zone. Feeding roots are found massed at this zone or just below it. DeKalb soil is apparently more aged, most acid, and lowest in base exchange capacity. The profile characteristics of these four soils confirm the data previously reported for nine northwestern forest soils by Powers (4).

The "F" layer of Aiken and of Olympic silty clay loam under Douglas fir [*Pseudotsuga taxifolia* (La Marck) Britt] forest cover contained approximately 9 and 13 tons an acre of organic matter respectively, where the whole corresponding forest floor was approximately 10 and 16 tons. The nitrogen content slightly exceeded 1 per cent in the "F" layers. Fine feeding roots are massed just below this in the surface of the A_1 layer, apparently taking up nitrates promptly. At the end of a protracted dry season, the moisture content of the "F" and "H" layers in Aiken and Olympic soil profiles averaged 19 per cent.

MICROÖRGANISMS IN FOREST SOIL PROFILES

Preliminary investigations of profiles from pine, fir, redwood, juniper and spruce forests show the prevalence of certain characteristics in common, regardless of soil or forest type (table 2). Litter in all cases had the highest water capacity and harbored great numbers of microörganisms; when moist it yielded higher counts than underlying layers. "F" and "A" horizons generally contained the greatest numbers of all classes of microörganisms. H-layers were not well developed; traces of H-material could often be found, but in most cases could not be adequately sampled. All litter and "F" layers were markedly acid; they also often yielded water-soluble phosphate and nitrate when these were absent in lower layers.

Molds were much less variable in numbers than bacteria and actinomycetes; this was true not only of the various horizons of a given profile, but also of different profiles. The most numerous molds were penicillia; mucors and aspergilli, although much less abundant, were next in order and increased proportionally with depth. DeKalb horizons from Pennsylvania hardwood forest gave contrasting results, in that molds were especially abundant, exceeding bacteria in both "F" and "H" layers, and actinomycetes were found only in the litter.

Incubation of profile samples moistened to one-half water-holding capacity for 2 weeks at 28°C. approximately doubled mold counts in "F" and "A_1" horizons, while in lower horizons the increase, though numerically small, was tenfold. Effects of incubation on bacteria and actinomycetes were irregular, but a reciprocal relation between these two groups was frequently exhibited. Moistening and incubating dry litter caused enormous increases in all microorganisms. Vigorous nitrification was found to proceed in the litter and "F" layers of a spruce profile. Nitrates were absent in the sample when collected. During storage in the natural moist condition, however, nitrates accumulated

until, after 17 months, the litter contained 2250 p.p.m. and the "F" layer 550 p.p.m. nitrogen as NO_3.

TABLE 2

*Microörganisms in forest soil profile**

SAMPLE	H_2O (WATER-FREE BASIS)	NUMBERS PER GRAM, WATER-FREE BASIS		
		Bacteria	Actinomycetes	Molds
	per cent			
1. *DeKalb* silt loam air dry samples of 4/23/32 *incubated* at 28° and approximately 1/2 saturation for two weeks 6/14/33				
Litter	566	4,320,000	2,520,000	2,398,000
F-layer	344	4,883,000	None	7,394,000
H-layer	212	9,570,000	None	13,200,000
A*	23.5	1,413,000	None	1,000,000
2. *Aiken Silt Loam*—field condition, not incubated				
Litter	35.1	13,600	13,600	129,200
F	70.9	1,208,000	490,000	315,000
H	62.6	11,573,000	261,000	293,000
A, 0–6″	33.7	667,000	95,000	65,300
A, 6–15″	34.6	3,672,000	612,000	53,000
B, 15–36″	33.9	2,448,000	1,360,000	19,000
C, 4–4½″	39.5	392,000	10,000	1,600
3. *Olympic Silt Loam*—field condition, not incubated				
Litter	25.0	66,780,000	882,000	10,100
F	223	47,538,000	11,628,000	85,500
H	223	34,542,000	9,234,000	171,000
H, transition	147	7,627,000	4,734,000	65,800
A_1	6.9	1,980,000	642,000	37,500
A_2	31.9	4,323,000	732,000	12,000
B	38.9	596,000	78,000	1,400
C	63.4	175,000	80,000	3,000

* No Azotobacter found in A.

EARTHWORMS AND OTHER MACROÖRGANISMS

A large species of earthworm and also moles and pocket gophers were observed to be active in cut-over and in forested land. Darwin (2) estimated that in England, 0.22 acre-inch passed through the body of earthworms a year and that the number of earthworms in some English soils was approximately 27,000 an acre. Bear (1) reported approximately 1,000,000 an acre in Ohio soil.

The number of earthworms based on several tests for western Oregon soils affected by tree cover was estimated. In Sites silty clay loam from which Douglas fir had been cut, the earthworms numbered approximately 250,000

an acre. In Willamette silty clay loam, under soft maple, they were estimated at 500,000 and in newly cultivated soil manured the year previous, earthworms were found present at the rate of approximately 1,500,000 an acre. Soil erosion plats on this soil type 0.001 acre in area, lost from 50 to 132 earthworms into the catch cans in a 3-months' period beginning February 12, 1935.

Earthworm castings were found in the fir forest under the litter in the crumb-mull on top of the mineral soil. The castings were collected from the surface on cut-over land where there was little litter. Chemical tests of earthworm castings and related materials are shown in table 3.

The work of earthworms appears to have little effect on reaction. There is evidence of a build-up in base exchange capacity, and the nitrogen and organic matter are much higher in the casting than in the parent soil.

TABLE 3

*Chemical characteristics of earthworm castings and related materials**

	MAPLE AND GRASS LITTER	SOIL	CASTINGS
From Willamette silty clay loam—under soft maples, collected O. S. C. Campus, 3/4/35:			
Reaction value, pH	6.74	6.50	6.80
Base exchange capacity, *m.e. per 100 gm.*	34.50	7.68	8.91
Organic matter, *per cent*	67.50	3.17	9.02
Total nitrogen, *per cent*	0.994	0.150	0.397
From Sites silty clay loam—cut-over fir land. NE. Q. Sec. 10, Tp 13 S; R 6 W Wm Mer Ore.:			
Reaction value, pH	6.7	6.20	6.20
Base exchange capacity, *m.e. per 100 gm.*	14.30	11.40	27.13
Organic matter, *per cent*	73.14	6.52	34.66
Total nitrogen, *per cent*	.....	0.228	0.672

* Mr. Clarence Burnham, research fellow in soils, assisted in these determinations.

Earthworms and related macroörganisms serve as colloid mills to generate an intimate mixture of fine organic and inorganic matter. To test the value of their activity, duplicate series of jars of loam were arranged with water jackets to confine earthworms. Two jars were used as checks; a second pair received earthworms; a third pair, worms and green clover clippings; and a fourth, clippings only.

Barley grown in these jars yielded definitely more where the worms were at work. Other culture jars of sandy loam to which earthworm castings were added to the amount of 5 per cent dry weight show growth response indicating that the beneficial effect is partly chemical.

NITROGEN AVAILABILITY IN FOREST SOIL LAYERS

A study was made of the nitrate-supplying power of two forest soil profiles by adding sufficient material from each horizon to supply 1.5 gm. nitrogen to

TABLE 4

Nitrogen availability in forest soil layers

Determinations started January 27, 1932

FOREST SOIL	TREATMENT OF 3,800 GM. SAND	NITROGEN IN LITTER	MATERIAL REQUIRED FOR 1.5 GM. N	OAT HAY PRODUCED		N TOTAL	NITROGEN REMOVED IN CROP
				Fresh	Dry		
		per cent	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
Astoria fir land	Litter	0.989	152.00	34.94	10.48	0.609	0.0638
	F layer	1.199	125.10	43.20	12.96	0.652	0.0845
	H layer	0.655	229.00	43.25	12.97	0.536	0.0695
	H-S	0.293	511.00	66.75	20.02	0.553	0.1107
	Soil	0.155	967.00	3.95	1.18	0.815	0.0096
	Solution, N	.....	.....	2.57	0.77	0.848	0.0065
	$NaNO_3$	16.000	9.37	.....	.....	.....	.....
	$(NH_4)_2SO_4$	20.000	7.50	.....	.....	.....	.....
	R. Blood	12.000	12.50	.....	.....	.....	.....
	Complete solution			100.13	30.04	0.695	0.2088
Pioneer camp, Ponderosa pine land	Litter	1.060	141.50	23.90	7.17	0.599	0.0429
	F	1.177	127.00	18.50	5.55	0.506	0.0281
	H	0.861	174.00	43.68	13.10	0.498	0.0652
	H-S	0.179	836.00	10.31	3.09	0.465	0.0609
	Soil	0.092	1633.00	43.40	13.02	0.389	0.0506
	Solution, N	.....	.....	4.20	1.26	0.822	0.0104
	$NaNO_3$	16.000	9.37	.....	.....	.....	.....
	$(NH_4)_2SO_4$	20.000	7.50	.....	.....	.....	.....
	R. Blood	.....	12.50	.....	.....	.....	.....
	Complete solution	.....	.....	94.27	28.28	0.579	0.1637

TABLE 5

Nitrate in leachate from fallowed percolation tubes

(Soil layers—1,900 gm. sand + 0.75 gm. N in forest-floor layers)

	FEBRUARY 10	FEBRUARY 22	MARCH 7	MARCH 20	TOTAL NITROGEN LEACHED, 6-WEEK PERIOD
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
Astoria + 1,900 gm. sand:					
Litter 76 gm.	2.4	3.5	1.5	2.0	9.4
F 62.5	2.8	2.0	0.4	Trace	5.2
H 114.5	2.5	0.7	0.2	Trace	3.4
HS 225.0	0.5	0.1	0.3	Trace	1.0
Sand X-1,900	Trace	0.0	0.0	0.0	Trace
L 76 + 40. $CaCO_3$	3.0	3.0	0.5	2.5	9.0
Pioneer camp + 1,900 gm. sand:					
L 70.7	2.0	3.7	0.6	1.00	7.3
F 63.7	1.3	0.1	0.4	1.00	2.8
H 87.0	1.0	0.2	0.4	2.00	3.6
H-S 41.0	0.5	2.5	0.4	1.12	4.6
Sand X 1,900	Trace	Trace	0.0	0.00	Trace
L 70.7 gm. + 40 gm. $CaCO_3$	7.5	2.0	0.5	0.63	9.6

culture jars containing 3,800 gm. of clean quartz sand. A culture solution lacking nitrogen was used to help keep the sand moist while oats were grown. The yield and nitrogen content were determined as shown in table 5. The maximum crop yield and nitrogen content were obtained where nitrogen was supplied in material from the H or H-S layer (see plate 1).

Parallel series of large glass percolation tubes were similarly prepared except that they were fallowed and leached each 2 weeks, and the nitrate in leachate was determined as reported in table 5. Copper sulfate proved most suitable for clarifying solutions for colorimetric determinations, which, however, are only approximate. Liming increased yield of nitrate slightly. Relative amounts of nitrate correspond to yields and nitrates removed in the cropped series. The writers plan a further study of the nitrogen economy of forest soils.

DISCUSSION

Data herein presented support those previously reported by Lunt (3) and show that the maximum absorptiveness for moisture or colloidality, maximum adsorptiveness or base exchange capacity, and maximum number of microorganisms and macroörganisms were found in the fermenting layers which contain approximately 75 per cent organic matter. Artificial mixtures of organic and inorganic soil colloids, varied by 20 per cent intervals, show a corresponding base adsorption curve.

The forest soil profiles from Pennsylvania, being more acid and lower in base exchange capacity, show more degeneration than do those from the Pacific Northwest.

The earthworms and related macroörganisms serve as colloid mills to generate this intimate mixture of fine organic and inorganic matter.

Feeding roots are massed in forest soils in or just below this organic layer. Lunt (3) has reported that 40 to 45 per cent of the exchangeable calcium in the whole profile is found in the humus portion, or the A1 horizon. Active organic matter may increase the soluble iron and perhaps phosphorus in the soil solution.

SUMMARY

Studies of forest soil profiles made at the Oregon Experiment Station show that the nutrient supplying power is centered in the F and H layers, especially as to bases and nitrates. Microörganisms and also macroörganisms are important in humus-nitrogen generation.

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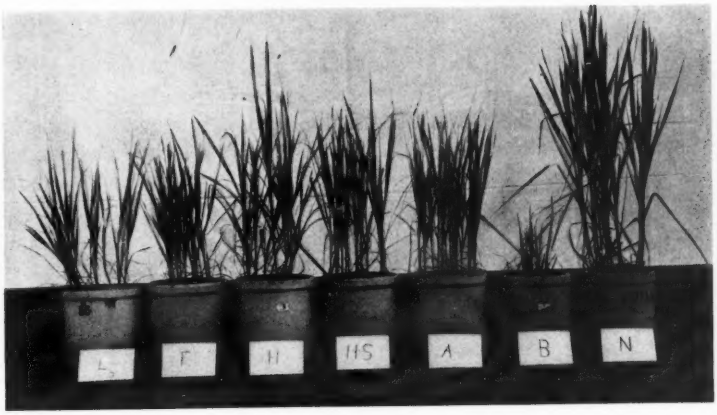
PLATE 1

GROWTH OF OATS IN SAND CULTURES KEPT MOIST WITH CULTURE SOLUTION LACKING NITROGEN, AND SUPPLIED WITH 1.5 GM. NITROGEN IN FOREST SOIL LAYERS

"Complete" nutrient solution at right

PLATE 1



MICROBIAL ACTIVITIES IN SOIL: II. ACTIVITY OF SPECIFIC GROUPS OF MICROBES IN RELATION TO ORGANIC MATTER TRANSFORMATION IN PALOUSE SILT LOAM[1]

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Although climatic environment and inherent soil characteristics are primary factors in controlling the biological activity in soil, the nature and quantity of potential food supplied by organic residues readily modify this activity. The profuse evolution of carbon dioxide and the sudden increase in number and activity of many different kinds of organisms following additions of organic residues to the soil have been the subject of extensive investigations, but the rôle of specific groups of microbes in relation to the activity of other groups and to the progressive steps in the process of organic matter transformation in the soil is not well known.

In the decomposition of straw by a mixed soil flora Norman (5) recognized the fact that there is a sequence in types of organisms. Waksman and Starkey (11) are of the opinion that frequently there is a sequence of organisms depending upon the nature of the organic residues as a source of energy. Results given in a previous publication (8) suggest that in the transformation of carbonaceous residues added to the soil there is a definite sequence of activity of important groups of microbes which appears to affect the development of other groups. The following data are presented in an attempt to elucidate further the activity of specific groups of microbes and their functions in the progressive steps in the transformation of organic residues in the soil.

EXPERIMENTAL PROCEDURE

Unpublished data from three of a series of continuous wheat plots $\frac{1}{27}$ acre in size and receiving the indicated field treatments for nine consecutive years show the following results[3]:

[1] Published as Scientific Paper No. 258, College of Agriculture and Agricultural Experiment Station, State College of Washington.

[2] Professor of soils and research assistant, respectively.

[3] The authors are indebted to the late H. F. Holtz for the data on these plots.

FIELD PLOT	ANNUAL TREATMENT PER ACRE	AVERAGE YIELD OF WHEAT PER ACRE	GAIN IN N PER ACRE,* EXCLUDING N ADDED BY FERTILIZER AND N REMOVED BY CROP
	pounds	*bushels*	*pounds*
104	Stubble returned	23.4	124.6
105	Straw 2700 $NaNO_3$ 370	34.5	1.3
107	Straw 2700 $(NH_4)_2SO_4$ 286	31.6	376.9

* Based on 3,500,000 pounds of dry soil.

The different behavior of the nitrogen and consequently of the organic matter in the soils of the two plots receiving the same amount of straw and also the same amount of nitrogen which, however, was supplied in different forms of fertilizer, prompted this investigation.

Preparation of Soil Samples.—In July, 1930, when the soil moisture content in the root zone approached the wilting point, representative samples of soil were obtained from each plot. Borings 1 foot deep were made with a soil auger at 48 points uniformly distributed on each plot, and sufficient soil was thus obtained to make the samples equivalent to 8 kgm. of dry soil. These were passed through a 6-mesh sieve several times to insure thorough mixing and to remove coarse organic residue. The soils were placed in jars, to which sufficient water was added to adjust the moisture to the normal field capacity of 20 per cent. The jars were covered and allowed to stand in the laboratory for 4 days to insure uniform moisture distribution and to give the microflora a chance to resume its normal functions. The soils were then removed from the jars and divided into two equal portions. One per cent finely ground wheat straw reenforced with enough ammonium nitrate to make the nitrogen content of the straw equivalent to 2.5 per cent was thoroughly mixed with one of each of the duplicate portions. Since a preliminary examination indicated that the number of Azotobacter in the field soil was small, each sample was inoculated with a heavy suspension of these organisms. A quantity equivalent to 1 kgm. of dry soil was removed from each sample for chemical and microbial analyses, and the remainder was placed into wide-mouth bottles and packed by gently jarring the bottles on the table. The bottles were connected with an absorption train for carbon dioxide determinations. The arrangement of the samples and soil treatments was as follows:

FIELD PLOT	FIELD TREATMENT PER ACRE	SOIL SAMPLE	LABORATORY TREATMENT PER KILOGRAM DRY SOIL
	pounds		*gram*
104	Stubble returned	1	Control
		2	Straw, 10 NH_4NO_3, 0.68
105	Wheat straw, 2700 $NaNO_3$, 370	3	Control
		4	Straw, 10 NH_4NO_3, 0.68
107	Wheat straw, 2700 $(NH_4)_2SO_4$, 286	5	Control
		6	Straw, 10 NH_4NO_3, 0.68

Determination of Microbial Activity.—The experiment was carried on at room temperature, which ranged from 20 to 25°C. The production of carbon dioxide and the numbers of total bacteria, fungi, actinomyces, cellulose decomposing bacteria, and Azotobacter were determined at the beginning; after the first, second, fourth, seventh, eleventh, and sixteenth day of the experiment; and every week thereafter until the end of the fifteenth week, when the microbial activity remained relatively uniform and the interval between determinations was extended to 2 weeks.

The numbers of total bacteria were ascertained by the direct microscopic method, and those of the fungi, cellulose decomposing bacteria, and Azotobacter, by plating on selective media following essentially the same procedure as described in a previous publication (8). The numbers of actinomyces were determined by plating suitable dilutions of soil suspensions on albuminate agar media prepared according to Fred and Waksman (2) and adjusted to pH 8.0.

The samples for the determination of microbial development were prepared in the following manner: At each sampling the soil from each bottle was removed and passed three times through a 6-mesh sieve onto a clean paper. This procedure was considered helpful in producing a thoroughly mixed, representative sample and in promoting thorough aeration, which should prevent the occurrence of any possible anaerobic condition that otherwise might develop in the bottles during the course of the experiment. The small amounts of soil required for plating were weighed immediately, and those needed for the silica gel plates were air dried by spreading them thinly on clean papers. The remainder of the soil was returned to the bottles and packed by gently tapping the bottles on the table. The soil moisture content was maintained within narrow limits by addition of water when necessary.

Chemical Analysis.—Chemical analyses were made at intervals for soil reaction; organic carbon; total nitrogen; nitrate nitrogen; fats, waxes, and resins; hot-water-soluble substances; hemicelluloses; cellulose; protein; and lignin. These substances were determined: A, at the beginning of the experiment; B, 37 days later when the fungi had reached the peak of activity; C, at 100 days when the maximum activity of the Azotobacter had been reached; and finally D, at the end of the experiment. The samples for these analyses consisted of quantities equivalent to 1000 gm. of dry soil for the first period and 800 gm. of dry soil for the other periods. These samples were air dried and stored until it was convenient to analyze them consecutively.

The total and nitrate nitrogen contents were determined by the Kjeldahl and phenoldisulfonic acid procedures respectively according to the official and tentative methods of analysis (1); the organic carbon contents, by the wet combustion method of Friedemann and Kendall (3); and the pH values, by means of the quinhydrone electrode in suspensions of one part of soil to five parts of water. The fractionation of the organic matter was conducted according to the method outlined by Waksman and Stevens (10).

EXPERIMENTAL RESULTS

The trend of CO_2 production and of the activity of various groups of microbes is illustrated in figures 1, 2, and 3. As can be noted, the addition of 1 per cent wheat straw to soils which were assumed to be normal in microbial activity at the time this organic residue was applied caused an immediate profuse production of CO_2 and a somewhat delayed but nevertheless great increase in numbers of bacteria, fungi, and actinomyces. Whereas the production of CO_2 was greatest the first day, the increase in numbers of microbes lagged considerably and did not reach a maximum until about one month later when the production of CO_2 was relatively low. A similar occurrence has been observed previously (8).

It may be assumed that as the microbial cells multiplied, more of the liberated CO_2 was used up by the rapidly increasing population. This might account for a brief lag period between CO_2 production and multiplication of organisms, as a part of the new food supply was probably used up before active multiplication of microbial cells took place. It does not explain the protracted lag which extended over a period of several weeks. CO_2 production and numbers of organisms did not occur in comparable proportions as long as considerable quantities of readily available organic compounds were present. Not until the decomposition of the straw had proceeded far enough to approach the conditions existing in soils 2, 4, and 6 was a relatively stable equilibrium reached in the activity of the important groups of microbes primarily concerned with the transformation of organic matter. Evidently the rate of CO_2 evolution cannot always be considered as a true index of the numbers of organisms at work.

The bacteria as a group were the quickest to take advantage of the readily available food supply, but they were followed very closely by the actinomyces in two of the three soils. Since the number of fungi did not rise materially during the first four or five days, it would seem that they were unable to compete successfully with the other groups at that time. The fungi may have been very active, however, with resulting increase in size of colonies and extent of mycelium, which is very difficult to detect by plant count.

The activity of cellulose decomposing bacteria and Azotobacter was not appreciably affected by the additions of straw and soluble nitrogen until the numbers of bacteria, actinomyces, and fungi were distinctly on the decline; that is, about 50 to 60 days after the experiment was started. Hence, the cellulose decomposing bacteria, in as far as numbers are concerned, were relatively inactive while the supply of cellulose was greatest and reached their peak of activity only after the competition of the more vigorous groups had abated and a large part of the cellulose had been decomposed. Even then their numbers failed to reach important proportions.

Parallel with the development of cellulose decomposing bacteria was that of Azotobacter which, like the former, failed to reach large numbers. Both

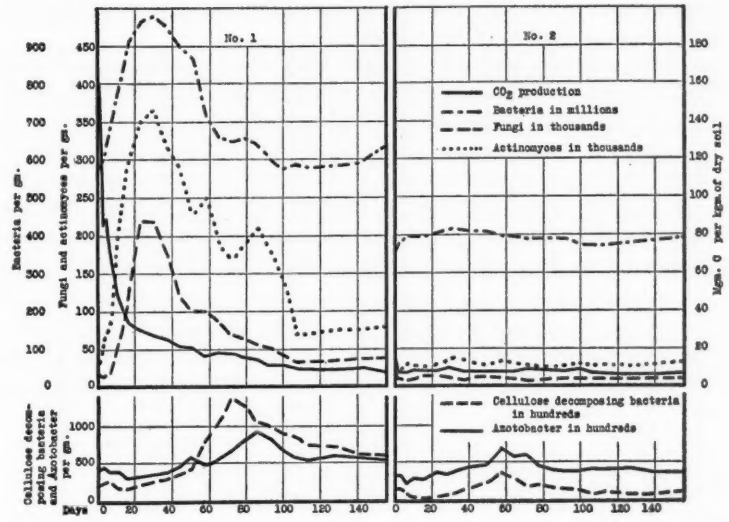

FIG. 1. CO_2 PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL TO WHICH STUBBLE ONLY WAS RETURNED FOR 9 CONSECUTIVE YEARS

No. 1, soil treated with 1 per cent straw supplemented with NH_4NO_3; No. 2, control

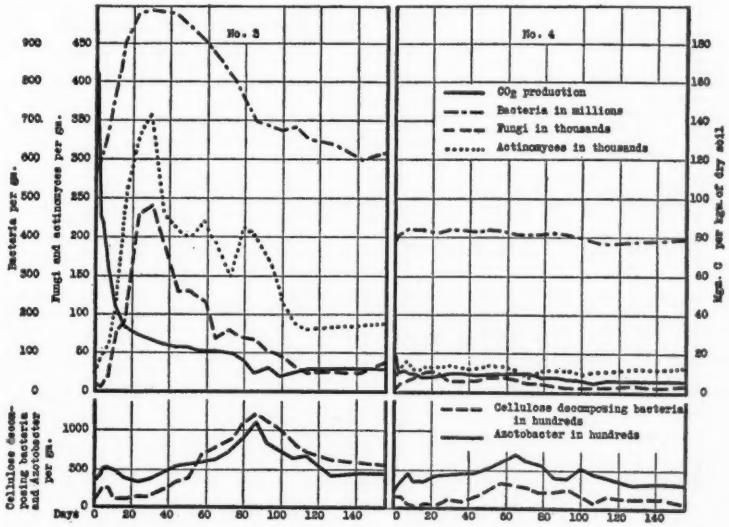

FIG. 2. CO_2 PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL RECEIVING 2,700 POUND OF STRAW AND 370 POUNDS NITRATE OF SODA ANNUALLY FOR 9 YEARS

No. 3, soil treated with 1 per cent straw supplemented with NH_4NO_3; No. 4, control

of these groups appeared to be better able to utilize the more resistant parts of the straw than the three other groups.

One of the objects of adding large quantities of straw to soils 1, 3, and 5 was to study the effect of this carbonaceous residue on the development of Azotobacter and incidentally on non-symbiotic nitrogen fixation. A previous study (8) has revealed that the activity of Azotobacter both in terms of numbers and in terms of nitrogen fixation may be stimulated conspicuously when the soil has received large quantities of cellulose and other organic residues. The results were obtained on soils taken from the field at a time when Azotobacter was very active. Data in another publication (7) indicate that there

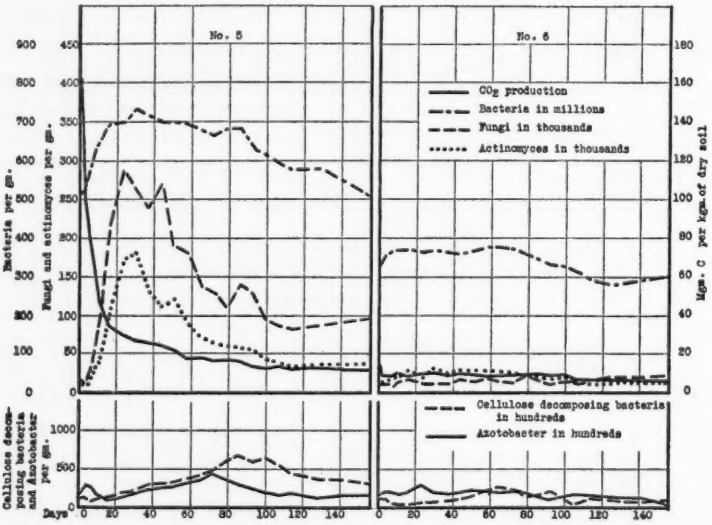

FIG. 3. CO_2 PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL RECEIVING 2,700 POUNDS OF STRAW AND 285 POUNDS SULFATE OF AMMONIA ANNUALLY FOR 9 YEARS

No. 5, soil treated with 1 per cent straw supplemented with NH_4NO_3; No. 6, control

was considerable fluctuation in numbers of Azotobacter in field plots lying adjacent and receiving similar treatments to the ones used for the work here presented. As has been stated already the number of Azotobacter in the latter soils was small and inoculation with an active suspension of these organisms was necessary. In spite of this inoculation and contrary to previous results (8) the number of Azotobacter never reached sufficient proportions to fix significant amounts of atmospheric nitrogen. The data in table 1 actually show a loss of nitrogen in two of the three samples that had been treated with 1 per cent of straw. The control samples, on the contrary, gained in total nitrogen, but this gain cannot be attributed to the activity of Azotobacter.

The curves in figures 1, 2, and 3 (samples 2, 4, and 6) indicate that the

repeated field applications of wheat straw and nitrogen fertilizers did not significantly affect CO_2 evolution or the activity of various groups of microbes. This is confirmed largely by the data in table 1, showing that no important quantities of organic matter have accumulated as a result of these treatments. The small increases occurring can be accounted for by the partially decomposed residue which no doubt accumulated under the existing climatic conditions.

Although the total CO_2 production, as shown in table 1, was greatest in sample 5 (the soil which had received ammonium sulfate and straw in the field), the microbial activity proved to be less than in either sample 1 (the soil receiving only stubble in the field) or sample 3 (the soil treated with straw and sodium nitrate in the field), in so far as could be ascertained by total numbers in the groups of organisms studied. Furthermore, the microbial activity in sample 5 was of a different nature. The numbers of bacteria and actinomyces were consistently lower and the numbers of fungi considerably higher than in

TABLE 1

Carbon dioxide production and organic carbon and nitrogen balance

SOIL	C		LOSS	N		LOSS OR GAIN	C PER KGM. OF DRY SOIL
	Beginning	End		Beginning	End		
	per cent	*per cent*	*lbs.**	*per cent*	*per cent*	*lbs.**	*gm.*
1	2.25	2.01	8400	0.153	0.148	−175	2.24
2	1.70	1.56	4900	0.153	0.156	+105	1.29
3	2.33	2.08	8750	0.156	0.156	00	3.41
4	1.77	1.58	6650	0.156	0.165	+315	1.58
5	2.32	2.10	7700	0.161	0.156	−140	3.44
6	1.85	1.67	6300	0.161	0.180	+665	1.34

* Based on 3,500,000 pounds of dry soil.

the other two samples. The same tendency prevailed in sample 6 (soil from the same plot) but to a much smaller degree, because it had not received the 1 per cent straw in the laboratory. Under certain soil conditions the favorable growth of fungi, such as occurred in sample 6, might be expected to result from increased acidity which is often brought about when ammonium sulfate is applied repeatedly. Such an explanation does not hold in this case, as the pH values of samples 5 and 6, as indicated in table 2, were greater than those of the soil to which stubble alone had been added. Since the only apparent chemical difference in this soil as compared with the others is a possible accumulation of sulfate compounds, it seems reasonable to assume that the residual effect of sulfate may account for the observed difference in biological activity. Thus it appears that specific soil characteristics either inherent or brought about by soil management may have a determining effect upon the particular nature of the prevailing microbial activity even though the original food supply is the same.

Regardless of the variation in nature of microbial activity, it is evident that

during the first stages of organic matter transformation following the addition of 1 per cent straw the production of CO_2 was not a true index of microbial propagation. These first stages of decomposition were marked by a distinct sequence of organisms with the bacteria as a group taking the lead, followed closely by the actinomyces and the fungi respectively in two of the three soils, and by the actinomyces and fungi simultaneously in the other soil. The cellulose decomposing bacteria and Azotobacter did not increase in numbers materially until the activity of the three other groups had subsided.

FUNCTIONS OF SPECIFIC GROUPS OF MICROBES IN ORGANIC MATTER TRANSFORMATION

Tenney and Waksman (6) have shown that aerobic decomposition of plant residues takes place in definite steps depending upon the chemical composition of the materials. Unlike the majority of plant residues in which the hemicelluloses and celluloses usually make up the largest fraction, soil organic matter is low in these constituents and the lignins and proteins constitute the largest part. When undecomposed plant residue is added to the soil in field practice, it usually amounts to a relatively small percentage of the soil organic matter and is always a small proportion of the entire soil mass. Therefore, methods in organic matter fractionation that can be depended upon to give satisfactory results in showing the steps in the transformations of plant residue decomposing by itself without being mixed with soil can at best give only approximate results when used to determine the course of transformation of plant residue added to the soil in amounts consistent with field practice. Nevertheless, as is shown by the data in table 3, periodical determinations of various organic complexes during the process of organic matter transformation in soil indicate certain definite trends.

TABLE 2

Soil reaction and nitrate nitrogen accumulation

SOIL	pH VALUES		NO_3 IN P.P.M. OF N			
	Beginning	End	A 0 days	B 37 days	C 100 days	D 156 days
1	6.5	6.4	39	13	46	67
2	6.5	6.5	13	12	29	33
3	7.2	7.0	57	30	65	46
4	7.2	7.0	13	24	38	37
5	6.6	6.5	53	50	90	97
6	6.6	6.5	13	26	49	66

An examination of these data reveals marked changes in some constituents of the organic matter. At the beginning of the experiment the percentage of hot-water-soluble substances in the organic matter of the soils receiving 1 per cent straw was about twice as large, and that of the hemicelluloses and

celluloses more than twice as large as the percentage of these materials in the control soils. This comparison shows how the soil organic matter constituents may be affected when plant residues are returned to the soil and gives an idea of the magnitude of work that is to be performed by the microbes whose function it is to restore the equilibrium of these constituents to its original status.

The other extracts which contain the fats, waxes, and resins constitute only a small fraction of the organic matter, and it can be noted that the percentage of these constituents was not materially affected by soil treatments or by microbial activity.

During the first 37 days of incubation the carbohydrate compounds, including sugars, starches, hemicelluloses, and celluloses, contributed by the straw disappeared rapidly, whereas there was a slight increase in percentage of lignins and proteins. In the course of the following two months when the activity of bacteria, actinomyces, and fungi was on the decline and the cellulose decomposing bacteria and Azotobacter were in their most active stage the hot-water-soluble substances began to accumulate in two of the three soils. The hemicelluloses and celluloses continued to disappear rapidly, whereas the relative amounts of lignins and proteins continued to rise. The last period covering about two months was marked by a relatively small decline in numbers or organisms in each of the five groups. The relative proportion of water-soluble materials in the organic matter continued to increase, whereas the hemicelluloses and celluloses continued to disappear. The percentages of lignins and proteins also continued to increase, the former on account of its resistance to decomposition and the later as a result of protein synthesis by microörganisms.

The behavior of various organic complexes during the course of the organic matter transformation is well illustrated in figure 4, which is representative of the different soils employed. The trend in cellulose decomposition, which was similar in both the treated and control soils, is worthy of attention. In spite of the fact that the control soils maintained a very uniform microbial activity the percentage of cellulose in the organic matter dropped in a similar manner to that in the treated soils, which had a fluctuating microbial activity and were supplied with an abundance of cellulose in the form of straw. It should be noted in this connection that the soils employed for this work were obtained from plots supporting wheat that was approaching maturity. Hence, the control samples contained considerable amounts of fresh root tissue supplying readily available cellulose, and this may account for the behavior of cellulose in these samples. The gradual accumulation of hemicelluloses in the control soils is, as indicated in figure 4, in direct contrast with the behavior of these substances in the other soils and cannot be explained on the same basis as the behavior of the celluloses.

The steady increase in amounts of water-soluble material following the first 37 days' period of decomposition is of interest in that it occurred in the

control soils having a uniform microbial activity as well as in the treated soils under a fluctuating microbial activity and at a time when the numbers of bacteria, actinomyces, and fungi were dropping rapidly. Although the actual quantities of these substances are small in comparison with the total organic matter content, it seems that the bacteria, actinomyces, and fungi, which were quick in taking advantage of these compounds in the first stage of decomposition, would have prevented this accumulation if food relationships as stated by Waksman and Starkey (11) are the principal factors in the predominance of specific groups of microbes. There was no lack of available nitrogen to retard the growth of any of these groups, as can be seen from the

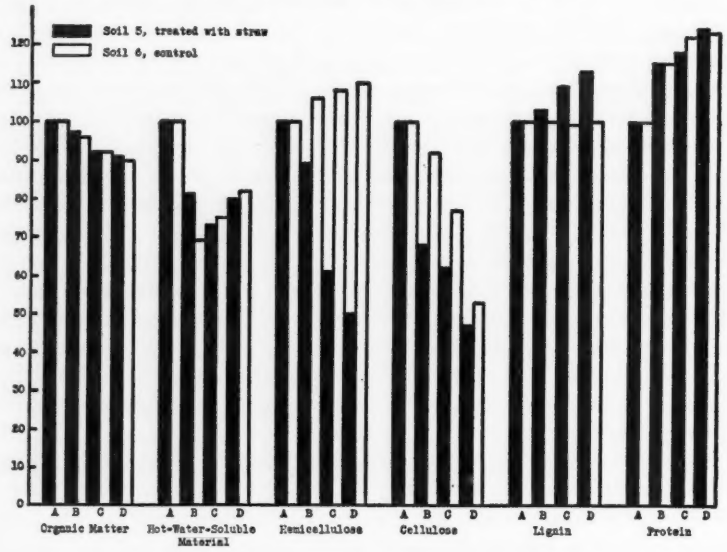

FIG. 4. TREND IN DECOMPOSITION OF ORGANIC COMPLEXES IN SOIL

A, beginning; *B*, 37 days; *C*, 100 days; *D*, 156 days

data in table 2. In all probability a large part of these accumulated products was of a secondary nature derived from microbial tissue and constituted less desirable food than the water-soluble substances in the plant residue. For similar conditions Norman (5) suggests that there is a production of toxic substances by specific groups of microbes which may result in a natural suppression of other groups.

From a comparison of the course of the various organic substances in the organic matter transformation as shown in table 3 and illustrated in figure 4 with the activity of specific groups of microbes in terms of numbers as indicated in figures 1, 2, and 3, it appears that the hot-water-soluble substances contributed by the straw were decomposed largely during the first 37 days and that

the bacteria as a group, because of their superior numbers and more rapid increase, were responsible for a large part of this decomposition.

The hemicelluloses and celluloses contributed by the straw appeared to be decomposed at a uniform rate during a period extending over approximately 80 days.

Heck (4) and Waksman and Skinner (9) attribute the principal rôle in the decomposition of cellulose materials to fungi. Judging from the numbers of

TABLE 3

Proximate composition of soil organic matter at various periods: A, beginning; B, 37 days; C, 100 days; D, 156 days of incubation

SOIL	ORGANIC MATTER	ORGANIC MATTER CONSTITUENTS*						TOTAL ACCOUNTED FOR
		Ether extract	Hot water extract	Hemi-cellulose	Cellulose	Protein	Lignin	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A1	3.88	1.88	7.06	6.56	9.66	28.66	40.30	94.12
2	2.93	1.23	4.44	2.94	4.11	31.62	48.63	92.97
3	4.01	2.01	7.07	6.34	10.62	29.33	40.82	96.19
4	3.06	1.57	4.05	2.68	4.11	30.73	47.44	90.58
5	4.00	2.44	8.09	7.18	8.65	28.12	41.68	96.16
6	3.19	1.66	5.64	3.10	3.24	31.73	49.15	94.52
B1	3.72	1.93	4.94	5.34	6.29	30.69	41.79	90.98
2	2.90	1.17	3.04	3.14	3.31	32.66	47.12	90.44
3	3.82	2.01	5.03	4.68	6.28	29.48	42.77	90.25
4	2.93	1.64	4.03	2.96	3.54	36.59	46.89	94.98
5	3.89	2.34	6.53	6.38	5.84	32.42	42.97	96.48
6	3.07	1.59	3.90	3.28	3.00	36.38	49.09	97.24
C1	3.52	2.10	5.79	3.56	5.19	33.08	44.16	93.88
2	2.76	1.30	3.47	3.28	2.62	35.79	47.19	93.65
3	3.67	1.93	5.88	3.30	5.83	33.90	44.18	95.02
4	2.82	1.87	5.67	3.02	2.56	37.97	46.28	97.37
5	3.70	1.94	5.89	4.40	5.36	33.13	45.34	96.06
6	2.94	1.46	4.22	3.34	2.51	38.62	48.82	98.97
D1	3.47	1.93	6.11	3.00	3.90	34.67	46.32	95.93
2	2.70	1.52	4.54	3.36	2.11	37.84	46.86	96.23
3	3.58	1.70	6.09	2.76	3.66	35.09	46.92	96.22
4	2.73	1.34	5.96	3.12	2.08	39.40	47.17	99.07
5	3.63	1.67	6.50	3.56	4.03	34.74	47.21	97.71
6	2.88	1.23	4.70	3.41	1.73	38.90	48.96	98.93

* Percentages on basis of dry organic matter.

organisms in various groups, it appears that the bacteria and actinomyces as well as the fungi took an important part in the decomposition of these products.

The activity of the cellulose decomposing bacteria and Azotobacter never became very prominent, but their numbers increased considerably after a large part of the readily available substances contributed by the straw had been decomposed, suggesting that these organisms are better able to utilize the more resistant compounds of organic residues than are the other groups.

The fact that the relative proportion of lignins to organic matter in the control soils remained uniform throughout the experiment, whereas it increased steadily in the treated soils is an indication that the lignin compounds supplied by the straw remained largely untouched during the course of the experiment.

SUMMARY

The activity of specific groups of microbes and their functions in organic matter transformation were studied in Palouse silt loam obtained from three of a series of field plots following nine years of continuous cropping with wheat. Stubble was the only residue returned to one of the plots, whereas the others received annual treatments of straw with sodium nitrate and of straw with ammonium sulfate respectively. One per cent of finely ground wheat straw reënforced with sufficient ammonium nitrate to make the nitrogen content of the straw equivalent to 2.5 per cent was mixed with one of the duplicate samples used from each plot.

Frequent determinations of the numbers of specific groups of organisms, including total bacteria, actinomyces, fungi, cellulose decomposing bacteria, and Azotobacter, and periodical analyses of various organic complexes were made in the laboratory.

During the first stages of decomposition of the organic residue in the soils the rate of CO_2 evolution was not a true measure of the numbers of active microbes, as the former was most profuse during the first days, whereas the latter did not reach their maximum numbers until about five weeks later.

A sequence of activity of specific groups of microbes occurred during this period. The bacteria as a group took the lead but were followed closely by the actinomyces and fungi.

The activity of the cellulose decomposing bacteria and Azotobacter never assumed important proportions. The largest numbers were reached after the activity of the three other groups had subsided, indicating that these organisms were better able to utilize the more resistant organic compounds in the straw than the other groups.

The repeated field applications of straw and nitrogen fertilizers did not affect CO_2 evolution and microbial activity to any appreciable extent.

The water-soluble substances contributed by the straw were decomposed largely in 37 days. The bacteria, because of rapid increase and superiority in numbers, were responsible for the major part of this decomposition.

The hemicellulose and cellulose compounds decomposed at a uniform rate during a period of approximately 80 days. The bacteria and actinomyces as well as the fungi took an important part in the decomposition of these products.

In the process of decomposition the protein content of the organic matter was steadily building up as a result of the rapid loss in carbohydrate materials and synthesis of protoplasm by the microbes.

The relative amounts of lignin in the treated soils increased gradually, in-

dicating that the major part of the lignin compounds supplied by the straw were not attacked by the microöorganisms during the course of the experiment.

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